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National Measurement Laboratory Center for Materials Science, Annual Report 1981

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Materials Science
Washington, DC 20234

November 1981

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NATIONAL MEASUREMENT LABORATORY CENTER FOR MATERIALS SCIENCE, ANNUAL REPORT 1981

John D. Hoffman, Director
National Measurement Laboratory

John B. Wachtman, Jr., Director
Center for Materials Science

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Materials Science
Washington, DC 20234

November 1981

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

ABSTRACT

The Center for Materials Science is part of the National Measurement Laboratory, one of the two principal laboratories comprising the National Bureau of Standards. The Center is organized in six Divisions, each having responsibility in different areas of materials science appropriate to the major classes of materials--metals, polymers, and ceramics and glass. The Divisions vary in their balance between theory and experiment, between direct standards work and research, and in their orientation toward industrial and Government needs and the needs of other components of the scientific and technical community. This volume summarizes the technical research activities and accomplishments of the six Divisions of the Center for Materials Science for fiscal year 1981.

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I. Introduction

The Center for Materials Science (CMS) was formed in 1978 as part of a general reorganization of the National Bureau of Standards. The Center is located within the National Measurement Laboratory (NML), one of the two principal laboratories comprising NBS. Figures 1, 2, and 3 (pp. 537, 538, 539) give the organization structure of the CMS, NML, and NBS, respectively. The CMS is one of the largest Centers at NBS. It has approximately 335 staff members; ~ 73 percent of the staff are professionals; of these, 67 percent hold Ph.D. degrees. The operating budget of the Center for FY81 amounted to ~ $23 M.

The long-term goal of the Center for Materials Science is to support the private sector and other Government agencies in the most effective application and utilization of materials--metals, polymers, and inorganic materials. Center activities in FY81 focused on those aspects of materials research involving processing science, structure/property science, and durability science. More specifically the Center

> Develops and maintains scientific competences and experimental facilities to provide the Nation with a central basis for uniform physical measurements, measurement methodology, and measurement services necessary to defining the properties and performance of materials and to other essential areas in the materials science discipline.
>
> Provides technical information in the form of reference data, materials measurement methods, and standard reference materials. Information is provided to other agencies of Government, universities, consumers, and to industrial processors, designers, and materials users to enable them to select cost effective combinations of materials, processes, designs, and service conditions.
>
> Characterizes the structures of materials, chemical reactions, and physical properties which will lead to the safe, efficient uses of materials, improve materials technologies, and encourage recycling.
>
> Obtains accurate experimental data on the behavior and properties of materials over time under service conditions to assure effective utilization of raw materials and manufactured materials.

The Center is organized in six Divisions, each having responsibilities in different areas of materials science. These Divisions vary in their balance between theory and experiment, between direct standards work and research, and in their orientation toward industrial and Government needs and the needs of other components of the scientific and technological community. The research activities of the Divisions are structured according to a task system; each task has specific goals, objectives, and milestones which support the overall goals of the Center. The following listing tabulates the tasks for each Division. Detailed descriptions of the FY81 technical activities encompassed by the various tasks are given in the following sections.

Task Numbers, Titles, and Leaders

Center Office		
12101	Microstructure of Materials	J. B. Wachtman, Jr.
Chemical Stability and Corrosion Division		
12111	Corrosion and Chemical Stability of Materials in Service Environments	T. D. Coyle
12112	High Temperature Chemical Stability and Process Chemistry	T. D. Coyle
Fracture and Deformation Division		
12121	Fracture and Deformation Mechanisms and Analyses	E. R. Fuller, Jr.
12122	Mechanical Durability of Ceramics and Composites	S. M. Wiederhorn
12123	Elastic-Plastic Fracture Mechanics	H. I. McHenry
Polymer Science and Standards Division		
12132	Polymer Standards for Control and Equity	I. C. Sanchez
12135	Tests, Standards, and Characterization for Manufacturing and Durability of Dental and Medical Materials	J. M. Cassel
12136	Mechanical Durability of Polymers for Design and Use	B. M. Fanconi
12138	Migration and the Durability of Polymers in Use	L. E. Smith
12139	Dielectric and Piezoelectric Plastics Design and Performance	M. G. Broadhurst
Metallurgy Division		
12142	Structure Characterization	M. Kuriyama
51105	Synchrotron Radiation Research for Materials Science	M. Kuriyama
12143	Metallurgical Processing	J. R. Manning
12144	Mechanical Properties and Wear	A. W. Ruff
12145	Chemical Metallurgy	R. Mehrabian
Ceramics, Glass, and Solid State Science Division		
12151	Structural Chemistry for Ceramic Processing and Durability	R. S. Roth
12153	Structural Methods for Processing Manufacture and Durability	S. Block
12154	Glass and Optical Materials	W. K. Haller
Reactor Radiation Division		
12161	Reactor Operation and Services	T. M. Raby
12162	Neutron Scattering Characterization of Materials for Advanced Technology	J. J. Rush
51102	Advanced Neutron Methods	J. M. Rowe
12163	Neutron Diffraction and Radiographic Methods for Materials Utility and Durability	J. J. Rush

CENTER FOR MATERIALS SCIENCE

OFFICE OF THE CENTER FOR MATERIALS SCIENCE

John B. Wachtman, Jr., Director
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The Center Office has the responsibility for providing the technical and administrative framework for the planning and operation of the technical programs carried out by the six Divisions and the Center Office scientists. Efforts this past year have focused on the development, strengthening, and implementation of programs and plans of the Center. Although the majority of the activities of the Center Office are reflected through accomplishments of the Divisions, several of particular interest merit mention here.

A Congressionally mandated study of the costs of fracture to the U.S. economy is being implemented by the Center. Operational supervision is by Dr. R. P. Reed of the Fracture and Deformation Division; the study will be completed in July 1982.

The Center has provided technical support to the Administration's activities on national materials policy. (1) The Department of Commerce response required by the National Materials and Minerals Policy Research and Development Act of 1980. Two major workshops were organized and held (see below) and initial drafts of three chapters of the Department's report on materials needs of the aerospace industry were prepared by CMS. (2) The Cabinet Council on Natural Resources and the Environment. CMS chaired the interagency Sub-working Group on Materials Research and Development and submitted a draft option paper to the Interagency Working Group on Strategic Minerals Policy.

The Center Director chaired the Committee on Materials (COMAT) Task Force on Federal Materials R&D that prepared the report "Materials Life Cycle Research and Development in the Federal Government, Fiscal Year 1980."

Center units have participated as organizer, sponsor, or host for the following meetings: (1) Fifth Annual Conference on Materials for Coal Conversion and Utilization, October 7-9, 1980; (2) U.S. Department of Commerce Public Workshop on Critical Materials Needs in the Aerospace Industry, February 9-10, 1981;

(3) Mechanical Failures Prevention Group, Innovation for Maintenance Technology Improvements, April 21-23, 1981; (4) Workshop on Conservation and Substitution Technology for Critical Materials, June 15-17, 1981; (5) Rapid Solidification Technology Briefing/Workshop, July 1-2, 1981 (COMAT).

Microstructure of Materials
Task 12101

Although most of the program planning and laboratory activity in the Center takes place in the Divisions, a single task, Microstructure of Materials, in the Center Office, takes a general view of materials science. This task supports cutting edge theory development basic to work in all Divisions and assures adequate attention to major new technical challenges and opportunities, particularly those that may affect two or more Divisions. The task provides senior consultation to the Department of Commerce and other agencies, to other NBS Centers, and to CMS Divisions, and thus provides a window on policy study in the Executive and Legislative Branches.

Fracture Theory
Subtask 1 of Task 12101

R. M. Thomson

A major review has been completed for the NATO Conference on the Atomistics of Fracture, entitled "Physics of Fracture." This paper is a current statement and assessment of atomistic theories and dislocation emission from cracks. The paper not only reviews our earlier work on one- and two-dimensional lattices, but develops a general contact with lattice Green's function theory, and outlines a general theoretical framework for a theory for all types of atomistic fracture problems. In the second half of the paper, we assess the current situation regarding dislocation emission at cracks. We have published the definitive theoretical paper on this subject (with Rice) a number of years ago, and much of the discussion of the Conference centered on theoretical and experimental questions concerning dislocation emission from cracks. This whole area is crucial for understanding the underlying brittle or ductile nature of fracture in materials.

A paper with Sinclair of Harwell explores new ground on the theory of dislocation interactions with cracks. The paper derives a basic theorem for the force on cracks and their dislocation screening clouds. This theorem is analogous to the J-integral, but does not have the limitations of J for moving cracks, and permits a theoretical structure to be developed for a fracture criterion which is suitable for microscopic fracture investigations.

A paper with Fuller to be published in the proceedings of the Pennsylvania State Fracture Conference pursues the more general Green's function approach mentioned above for two-dimensional lattices. We calculate lattice trapping energies for a variety of force laws, and derive the activation volume for these same cases. The theory demonstrates directly a decomposition theorem which allows discrete atomistic effects at the crack tip to be separated from the remaining linear response of the lattice. This decomposition result is shown to be closely related to the concept of a lattice Green's function for a crack. This paper shows in detail for the two-dimensional square lattice how the general Green's

function approach can be applied, and is part of our program to develop a theoretical basis for dealing with all types of atomistic fracture problems.

A joint review of status of fracture theory (jointly with Sinclair) explores current theoretical problems and assesses new approaches.

In collaboration with Lin of NBS, Boulder, we have nearly completed a new calculation of dislocation emissions from cracks when the dislocation Peiels energy is high. This result shows that the large Peiels energy of the dislocation allows emission to occur with much lower activation energies than calculated earlier. This result may explain an apparent low activation energy in silicon for dislocation emission which is otherwise difficult to understand. Again, in collaboration with Lin of NBS, Boulder, we have computed pileup configurations of dislocations in the vicinity of a crack using the full generality of the theory described above. Calculations such as this will help to develop fracture criteria for sharp cracks. This work is nearly complete.

In collaboration with John Hirth of Ohio State University, we have developed some general ideas about how to explain brittle transitions in ductile materials in terms of separate cleavage and emission criteria at the crack and the probability for reabsorption of virtually emitted dislocations. This work is still in a formative stage.

Theoretical Materials Stability
Subtask 2 of Task 12101

John W. Cahn

This work addresses fundamental factors in the stability of materials. It is carried on with a wide variety of colleagues.

In support of the phase diagram activity, statistical mechanical calculations of phase equilibria and ordering in hexagonal close packed metals have been carried out. The usefulness of various metastable curves on phase diagrams in predicting sequences of metastable equilibria and phase change mechanism has been explored. The usefulness of an exact thermodynamic equation for slopes of phase diagram curves as a tool for evaluating phase equilibria data has been explored.

A symmetry theory of crystal-crystal interfaces has been developed and applied to grain boundaries, stacking faults, antiphase boundaries, and to solid state phase transformations.

A solid-state thermodynamics theory has been developed which takes properly into account that surface or interface stress is different from surface or interfacial free energy.

The nature of the thermodynamic inequalities that arise for nonequilibrium surfaces has been explored. Examples far from equilibrium in which surface tensions are greater and smaller than equilibrium surface tensions have been given to show that careful control of conditions are required before a useful inequality can be guaranteed from thermodynamic principles.

Processes Involving Conformational Changes in Polymers
Subtask 3 of Task 12101

Darrell H. Reneker, J. Mazur

Relaxation processes in polyethylene crystals were investigated by modeling the migration of a defect called a point dislocation or twist dispiration loop as a stochastic process, governed by the Smoluchowski diffusion equation. The defect is driven along a straight polymer stem by fluctuating forces derived from thermal motions and by external forces derived from macroscopic strain. The defect passage causes both an axial transport of the molecule and a 180° rotation of the part of the stem traversed by the defect. The chain rotation is responsible for the observed dielectric relaxation and the narrowing of satellites of the C-13 line in the NMR spectrum. The defect motion is characterized by a diffusion coefficient and by the ratio, called the mobility, of the average drift velocity to the driving force. Calculations of first passage times associated with defect diffusional motion along appropriately defined routes lead to an estimate of the defect diffusion constant. A relaxation process occurs as defects diffuse from regions where the strain field increases the defect energy to regions where the strain decreases the defect energy. The model provides an estimate of the mechanical relaxation time and relaxation strength. The stochastic diffusion model for defect migration also provides a unifying viewpoint for interpretation of data from mechanical and dielectric relaxation experiments as well as from NMR experiments. It is attracting attention as a possible mechanism that limits the long time modulus of highly oriented polymer fibers. Currently the interactions between point dislocations and twist boundaries are being investigated, and the stochastic approach is being extended to analyze the thickening of folded chain lamellas.

The self diffusion coefficient of molten polyethylene measured with a magnetic field gradient nuclear magnetic resonance method is being compared with diffusion coefficients measured by observing the changes in concentration of perdeuterated molecules near a boundary between polyethylene and polyethylene containing per-deutero-polyethylene as a function of time. Current measurements suggest a surprisingly rapid local motion in polymer melts. This work extends the investigation of molecular transport by reptation into the melt. This work is being done in cooperation with collaborators in the Polymer Science and Standards Division and the Josef Stefan Institute in Ljubljana, Yugoslavia.

Energy minimization calculations are being used to investigate the effects of fold geometry and temperature on the overall energy of a single crystal. The results of these calculations are being correlated with observations of changes in crystal morphology which occur with increasing crystallization temperature.

Ultrasonic Imaging and Signal Processing
Subtask 4 of 12101

Melvin Linzer, Stephen J. Norton

A significant advance in ultrasonic imaging, the first exact three-dimensional inverse-scattering solution incorporating broadband illumination and based on variations in both compressibility and density was reported by Norton and Linzer. The problem was formulated and solved for three aperture geometries: plane, spherical, and cylindrical. Solutions were obtained under the assumptions of the Born approximation (i.e., weak scattering) and that only backscattering is measured.

An analysis and computer simulation of a new imaging system for acoustical holography, based on an annular aperture, was also completed. Additional work on image reconstruction was carried out in collaboration with T. Sato at the Tokyo Institute of Technology. This included tomographic reconstructions from limited projections using iterative revisions in image and transform spaces, and a data selection approach for imaging through turbulent media.

A theoretical development of perturbation techniques for correcting ultrasonic velocity images has also been carried out. This approach, which does not require ray tracing, is based on a Taylor expansion of the line-integral over the refracted path about the straight line connecting transmitter and receiver. The second term in this expansion is a correction representing the difference in the time delay over the refracted path and the straight path. This correction can then be used to modify the original line-integral measurements, which in turn can be used to reconstruct an improved image corrected for refraction errors. This approach gains little from iteration, and, because of its perturbation nature, may be assumed valid for velocity fluctuations within about ± 5 percent of the mean value, the range of velocity variation in most materials. In fact, computer simulations suggest that good results are possible for even larger variations.

Finally, an analysis of techniques for measuring ultrasonic parameters of materials was made and a manuscript on a sonic technique for detecting interrupted cutting during automated machining was completed.

Other Activities of the Office of the Center for Materials Science

Invited Talks

"Physics of Fracture
Brown University, Providence, Rhode Island
R. M. Thomson
September 1980

"Mechanical Properties of Crystalline Polymers"
University of Massachusetts, Amherst, Massachusetts
D. H. Reneker
October 1980

"Defects That Transport Polymer Chains Along Their Axis"
University of Tennessee, Knoxville, Tennessee
D. H. Reneker
October 1980

"Thermodynamics of Small Solid Particles"
University of Virginia, Charlottesville, Virginia
J. W. Cahn
October 13, 1980

"Wetting Transitions"
Massachusetts Institute of Technology, Cambridge, Massachusetts
J. W. Cahn
October 21, 1980

"Dislocation Screening of Fracture and the Force Theorem for Cracks
AIME Symposium on Fracture, Chicago, Illinois
R. M. Thomson
November 1980

"Rapid Solidification Processing"
Colorado School of Mines, Boulder, Colorado
J. W. Cahn
January 14, 1981

"Rapid Solidification Processing"
SERI, Boulder, Colorado
J. W. Cahn
January 16, 1981

"Department of Commerce Response to the National Materials and Minerals Policy, Research and Development Act of 1980"
Government and Public Affairs Committee of the American Society for Metals, Washington, D.C.
J. B. Wachtman, Jr.
February 5, 1981

"Department of Commerce Response to the National Materials and Minerals Policy, Research and Development Act of 1980"
Federation of Materials Societies, Board of Trustees/Advisory Board Meeting, Washington, D.C.
J. B. Wachtman, Jr.
March 31, 1981

"Advanced Materials Development: A Technological Response to the Critical Materials Challenge"
First Albany Corporation Workshop, New York, New York
J. B. Wachtman, Jr.
April 24, 1981

"Role of Interfaces"
Carnegie-Mellon University, Pittsburgh, Pennsylvania
J. W. Cahn
April 27, 1981

"Thermodynamics of Small Solid Particles"
Carnegie-Mellon University, Pittsburgh, Pennsylvania
J. W. Cahn
April 28, 1981

"Role of Interfaces"
Massachusetts Institute of Technology, Cambridge, Massachusetts
J. W. Cahn
April 30, 1981

"Physics of Fracture"
NATO Conference on Atomistics of Fracture, Corsica
R. M. Thomson
May 1981

"National Materials Policy: Critical Materials and Opportunities"
Annual Edward Orton Jr. Memorial Lecture, American Ceramic Society, 83rd Annual Meeting, Washington, D.C.
J. B. Wachtman, Jr.
May 4, 1981

"Critical Materials Needs of the Aerospace Industry: A Progress Report on the Department of Commerce Case Study"
American Defense Preparedness Association National Materials Policy Act (PL 96-479) Conference/Workshop, Fort Leslie J. McNair, Washington, D.C.
J. B. Wachtman, Jr.
May 5, 1981

"Recent Work in Ultrasonic Imaging"
Towson State University, Towson, Maryland
M. Linzer
May 5, 1981

"Properties and Performance of Materials"
Annual Dorn Lecture, Northwestern University, Evanston, Illinois
J. B. Wachtman, Jr.
May 12, 1981

"Symmetry of Crystal Crystal Interfaces"
IBM, Yorktown Heights, New York
J. W. Cahn
June 5, 1981

"Technical Activities at the National Bureau of Standards Related to Substitution and Conservation"
Workshop on Conservatin and Substitution Technology for Critical Materials, Vanderbilt University, Nashville, Tennessee
J. B. Wachtman, Jr.
June 17, 1981

"Charge to the Workshop on Conservation and Substitution Technology for Critical Materials"
Vanderbilt University, Nashville, Tennessee
J. B. Wachtman, Jr.
June 17, 1981

"Stochastic Model for Relaxation by Defect Motion in Polyethylene"
University of Groningen, Groningen, The Netherlands
D. H. Reneker
July 1981

""Activities and Plans of the National Bureau of Standards in Implementing Materials Policy Legislation"
Government and Public Affairs Committee, American Society for Metals, Washington, D.C.
J. B. Wachtman, Jr.
July 9, 1981

"Mechanical Relaxation Processes Caused by Defect Diffusion in Polyethylene"
American Chemical Society, New York
D. H. Reneker
August 1981

"Thermodynamic Properties of Surface and Interfaces"
International Conference on Phase Transitions on Surfaces, University of Maine, Orono, Maine
J. W. Cahn
August 1981

"Symmetry in Solid-Solid Transformation Morphologies"
International Conference on Solid-Solid Phase Transformation, Carnegie-Mellon University, Pittsburgh, Pennsylvania
J. W. Cahn and G. Kalonji
August 1981

Technical and Professional Committees and Leadership

Federation of Materials Societies

Committee on Materials Durability and Conservation
J. B. Wachtman, Jr., Chairman

Advisory Committee to Materials Research Laboratory, Pennsylvania State University
J. B. Wachtman, Jr., Member

Corporation Visiting Committee, Department of Materials Science and Engineering, Massachusetts Institute of Technology
J. B. Wachtman, Jr., Member

American Physical Society

J. B. Wachtman, Jr., Fellow
R. M. Thomson, Fellow
J. W. Cahn, Member

Committee on Applications of Physics
J. B. Wachtman, Jr., Member

Editorial Committee, Annual Review of Materials Science
J. B. Wachtman, Jr., Member

Mining/Metallurgy/Ceramics/Materials Engineering Peer Committee National Academy of Engineering
J. B. Wachtman, Jr., Member

Materials Science and Technology Committee
J. B. Wachtman, Jr., Member

Committee on Materials (COMAT)
J. B. Wachtman, Jr., Alternate Member

American Ceramic Society

J. B. Wachtman, Jr., Member
J. W. Cahn, Member
R. M. Thomson, Member

Executive Committee
J. B. Wachtman, Jr., Member

Rules Committee
J. B. Wachtman, Jr., Member

American Society for Testing and Materials

J. B. Wachtman, Jr., Member
D. H. Reneker, Member
R. M. Thomson, Member

American Chemical Society

J. B. Wachtman, Jr., Member
J. D. McKinley, Member

National Materials Advisory Board

Committee on Dynamic Compaction of Metal and Ceramic Powders
J. D. McKinley, Liaison Representative, NBS

Committee on Columbium and Tantalum Supply and Demand Outlook
J. D. McKinley, Liaison Representative, NBS

National Research Council

Solid State Science Committee
Committee on Applied Physics
R. M. Thomson, Member

Plastics Intitute of America

Research Committee
D. H. Reneker, Member

National Archives and Records Service

Advisory Committee on Preservation
D. H. Reneker, Member

Materials Research Laboratory, University of Massachusetts
D. H. Reneker, Member, Visiting Committee

Polymer Science and Engineering

Board of Editors
D. H. Reneker, Member

CRC Critical Reviews in Solid State Physics

Board of Editors
D. H. Reneker, Member

The Optical Society of America

Washington Area Drive for National Optics Center Fund
B. W. Steiner, Chairman

Technical Council
B. W. Steiner, Chairman

Executive Committee
B. W. Steiner, Member

Liaison with Society for Photo Optical Instrumentation Engineers
B. W. Steiner

American Institute of Metallurgical Engineers

Heat Treating Committee
J. W. Cahn, Member

Solidification Committee
R. M. Thomson, Member
J. W. Cahn, Member

National Academy of Engineering
J. B. Wachtman, Jr., Member

National Academy of Sciences
J. W. Cahn, Member

American Academy of Arts and Sciences
J. W. Cahn, Fellow
R. M. Thomson, Member

American Society for Metals
R. M. Thomson, Member

Thermodynamics Committee
J. W. Cahn, Member

Archeological and History Committee
J. W. Cahn, Member

Publications

Surface Stress and the Chemical Equilibrium of Small Crystals
I. The Case of the Isotropic Surface
J. W. Cahn and F. Larche
Acta Met. 28, 1333 (1980)

Eutectic Solidification and the Formation of Metallic Glasses
W. J. Boettinger, F. S. Biancaniello, G. M. Kalonji, and J. W. Cahn
Proc. Second International Conf. on "Rapid Solidification Processing: Principles and Technologies," R. Mehrabian, B. H. Kear, and M. Cohen, eds., Claitor's Publ. Div., Baton Rouge, Louisiana (1980), p. 50.

Metastable Equilibrium
J. W. Cahn
Proc. Second International Conf. on "Rapid Solidification Processing: Principles and Technologies," R. Mehrabian, B. H. Kear, and M. Cohen, eds., Claitor's Publ. Div., Baton Rouge, Louisiana (1980), p. 24.

Alloys in Metastable Equilibrium
J. W. Cahn
Bull. Alloy Phase Diagrams 1I, 26 (1980)

Obtaining Inferences About Relative Stability and Metastable Phase Sequences from Phase Diagrams
J. W. Cahn
Bull. Alloy Phase Diagrams 1, 27 (1980)

The Centennial of the Gibbs-Konovalov Rule for Congruent Points
D. A. Goodman, J. W. Cahn, and L. H. Bennett
Bull. Alloy Phase Diagrams 2, 29 (1981)

Mechanism for Diffusion Induced Grain Boundary Migration
R. W. Balluffi and J. W. Cahn
Acta Metall. 29, 493 (1981)

Ultrasonic Reflectivity Imaging in Three Dimensions: Exact Solutions for Plane, Cylindrical, and Spherical Apertures
S. J. Norton and M. Linzer
IEEE Trans. Biomed. Eng. BME-28, 202 (1981)

Tomographic Image Reconstruction from Limited Projections Using Iterative Revisions in Image and Transform Spaces
T. Sato, S. J. Norton, M. Linzer, O. Ikeda, and M. Hirama
Appl. Optics 20, 395 (1981)

Array Imaging System with Data Selection Processing
R. Sato, M. Linzer, O. Ikeda, and M. Hirama
J. Acoust. Soc. Amer. 70, XXX (1981), in press

Configurational Properties of Comb-Branched Polymers
F. L. McCracken and J. Mazur
Macromolecules 14, XXX, (1981), in press

Mechanical Relaxation Processes Caused by Defect Diffusion in Polyethylene
D. H. Reneker and J. Mazur
American Chemical Society Polymer Preprints, August 1981

Stochastic Defect Diffusion Model for Relaxation Effects in Crystalline Polyethylene
D. H. Reneker and J. Mazur
Polymer, in press

Critical Materials Needs for the Aerospace Industry
John B. Wachtman, Jr.
Resource Recovery and Conservation Magazine, 1981, in press

Proceedings U.S. Department of Commerce Public Workshop on Critical Materials Needs in the Aerospace Industry
John B. Wachtman, Jr., Editor
NBSIR 81-2305, to be published

Proceedings of the Workshop on Conservation and Substitution Technology for Critical Materials
John B. Wachtman, Jr., Editor
NBSIR 81-XXXX, to be published

Surface Stress and Chemical Equilibrium of Small Crystals. II. Solid Particles Embedded in a Solid Matrix
J. W. Cahn and F. Larche
Acta Metall., to be published

Tomographic Image Reconstruction from Limited Projections Using a Coherent Optical Feedback System
T. Sato, K. Sasaki, Y. Nakamura, M. Linzer, and S. J. Norton
Appl. Optics, 1981, to be published

Non-Equilibrium Surface and Interface Thermodynamics
J. W. Cahn
Proc. of NATO Conference on Fracture, Corsica, France, to be published

Comment on Chemical Potentials in Solids
J. W. Cahn and W. C. Johnson
Scripta Metall., to be published

Chemical Potentials in Solids: A Reprise
J. W. Cahn and W. C. Johnson
Scripta Metall., to be published

Symmetry in Solid-Solid Transformation Morphologies
J. W. Cahn and G. M. Kalonji
Proc. International Conf. on Solid-Solid Phase Transformation, Pittsburgh, Pennsylvania, to be published

Ultrasonic Tissue Characterization
M. Linzer and S. J. Norton
Ann. Rev. Biophys. Bioeng., submitted

A Sonic Technique for Detecting Interrupted Cutting During Automated Machining
F. P. Higgins and M. Linzer
J. Eng. Ind., submitted

Morphological Constraints on Crystals in Crystalline Environments
G. M. Kalonji and J. W. Cahn
Phys. Rev., submitted

Acoustical Holography with an Annular Aperture
S. J. Norton
J. Acoust. Soc. Amer., submitted

Special Reports

Report on Selected Critical Materials: Technical Impact on the Aerospace Industry
N. E. Promisel, Consultant
Prepared for National Bureau of Standards, U.S. Department of Commerce

Report on Federal Policy Options for Development Efforts in Regard to Critical Materials
Hamilton Herman, Consultant
Prepared for National Bureau of Standards, U.S. Department of Commerce

Honors and Awards

J. W. Cahn
Dickson Prize for Science
Carnegie-Mellon University, 1980

CHEMICAL STABILITY AND CORROSION DIVISION

CHEMICAL STABILITY AND CORROSION DIVISION (561)

Thomas D. Coyle, Chief
Samuel J. Schneider, Deputy Chief
L. L. Ware, Secretary
J. L. Inches, Secretary
W. M. Lambert, Student Aid
M. E. Lukens, Clerk Typist
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The chemical interactions of materials with their environment are critical to their durability and performance in service. The 1978 NBS-Battelle study on the Economic Costs of Corrosion showed that costs to the U.S. economy of metallic corrosion alone were 4.2 percent of the GNP in 1975. Chemical deterioration of organic and nonmetallic inorganic materials such as ceramics clearly adds a substantial additional burden to the economy. Moreover, the requirements of new technologies such as transportation, aerospace, and energy for materials that will operate at higher temperatures in aggressive environments demand chemically robust materials and the means to assess their performance and extend their service life.

The importance of materials-environment chemistry also extends beyond issues of durability. Materials processing by techniques ranging from electrodeposition to chemical vapor deposition to reaction sintering of advanced ceramics involve chemical transformations in which the role of the processing environment must be assessed and controlled. Further, this chemistry, particularly the way in which elements such as heavy metals enter and move in the environment, are critically important to the environmental impact of materials processing and use.

Within the overall program of the NBS Center for Materials Science, the Chemical Stability and Corrosion Division provides a focus for research and measurement activities related to the chemical stability and reactivity of materials in use and processing. The elements of the Division's program include: (1) research to establish mechanisms and models of corrosion and degradation processes, (2) determination of the chemical durability of materials, and (3) development of measurement methods in support of both research and testing. Mechanistic understanding, which includes the influence of environment and of materials composition and structure, is a basic requirement for improving materials durability. Characterizing performance provides the basis for selection of materials, development of improved materials, and the choice of control strategies. Measurement techniques are required both to assess performance and incipient failure of materials in service and to provide insight into molecular-level events needed to establish corrosion and degradation mechanisms.

The Division conducts numerous cooperative programs with both private sector and Government agencies, providing often unique services to those groups while maintaining the focus of the Division on problems of current technological concern. A long-standing program with the American Iron and Steel Institute (AISI) on corrosion protection of marine pilings is reaching completion and

will be replaced in the coming year with a new joint program on corrosion of pilings in landfills. A new program with the American Electroplaters' Society (AES) is investigating the use of pulsed electroplating processes to produce corrosion resistant alloy coatings which have the potential for reducing requirements for the use of critical alloying elements. A research associate program with the AES and the Aluminum Association is addressing fundamental aspects of electroplating on aluminum alloys. A joint program with the Electric Power Research Institute (EPRI) is developing *in situ* measurement methods to combat the growing problem of corrosion of buried electric power cables.

Joint programs with other agencies include several with the Department of Energy (DOE): corrosion behavior of container materials for nuclear waste storage; assessment of high temperature corrosion resistance of metals and metal-ceramic systems for downstream components of combined cycle magnetohydrodynamic (MHD) systems; experimental and modeling studies of slag chemistry for particulate and alkali control in coal combustion process streams; corrosion of metals for refuse-fired incinerator systems. With the Federal Highway Administration (FHWA) we are developing methods and a portable microprocessor-controlled instrument to measure corrosion rates of steel reinforcing bars in concrete bridge decks. At the request of the U.S. Navy, the Division is supporting the development of new organotin-based antifoulant hull coatings by developing methods to characterize the structures of the polymers to correlate with performance and by an extensive study of environmental fate and effects of the biocidal species leached from the coatings. Other activities are being carried out with the National Aeronautics and Space Administration (NASA) and the Rural Electrification Administration (REA).

Support of the NBS Standard Reference Materials (SRM) program is another important output. The Division produces and certifies SRM's (about 5000 units annually) for control of thickness coatings in the electronics, aerospace, paint, and other industries which use or produce coated materials. A dye-penetrant test block SRM to check the sensitivity of dye-penetrant NDE methods has also been developed. A new SRM for line position measurements in nuclear magnetic resonance (NMR) spectroscopy will be certified in the coming year. The Division's capabilities in microbiological deterioration mechanisms and trace-level characterization of metal-containing compounds is being used in a joint program with the Office of Standard Reference Materials (OSRM) to evaluate the stability of some compositional SRM's with respect to biodeterioration.

The Division has strong contacts to the voluntary standards community, and many staff members serve on ASTM, ANSI, and other bodies (see list at the end of this report).

The research activities of the Division, and its recent technical accomplishments, are described in the following pages. For management purposes, the technical program is divided into three task areas:

Task 12111	CORROSION AND CHEMICAL STABILITY OF MATERIALS IN SERVICE ENVIRONMENTS
Task 12112	HIGH TEMPERATURE MATERIALS STABILITY AND PROCESS CHEMISTRY
--	RECYCLED OIL PROGRAM--Division 561 Activities

The first task is largely concerned with chemical stability including metallic corrosion and biodeterioration processes in ambient environments. The second task focuses on chemical processes affecting materials durability and processing at high temperatures. The third area of work comprises work on the chemical properties and performance of lubricants in support of the NBS Recycled Oil Program.

CORROSION AND CHEMICAL STABILITY OF MATERIALS IN SERVICE ENVIRONMENTS
Task 12111

The technical focus of this task is the chemical interaction of materials with their service environments. Its overall objective is to promote the reduction of economic and environmental costs of corrosion and other forms of chemical deterioration. The work of the task provides data on the chemical durability (corrosion resistance) of materials, improved understanding of degradation mechanisms, new measurement methodology, and data and measurement methods for development and quality control of protective coatings. Through direct application of the results of the work, and through such mechanisms as participation of staff members in voluntary standards activities, these outputs support test method development, materials selection, corrosion control techniques, and improved technical practice leading to enhanced materials durability.

The technical activities of the task fall into two subtask areas. One subtask emphasizes metallic corrosion and protective coatings technology. The other subtask focuses on measurement and mechanistic aspects of chemically and biologically mediated processes (including microbial corrosion) which broadly affect the durability of metals and other materials as well as the environmental impacts of their processing and use.

Corrosion and Electrodeposition
Subtask 1 of Task 12111

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Technical activity in this subtask is aimed at providing a scientific base, data, measurement methodology, test methods, and standards to advance corrosion prevention and coating technologies. The group carries out this objective by work that ranges from test method development through field and laboratory studies of corrosion resistance of materials, to more basic investigations of corrosion mechanisms, and coatings science.

Corrosion Science, Measurement, and Test Methods. This area seeks to develop, improve, and evaluate test methods which will measure pitting, crevice, intergranular, and stress corrosion, hydrogen embrittlement, gaseous oxidation, underground, marine, and atmospheric corrosion in order to provide industry and Government with improved test methods. To accomplish these objectives, the approach is to apply the newest techniques provided by electrochemistry, metallurgy, surface physics, and chemistry to a study of corrosion processes and to eventually develop from these studies more effective techniques that can be applied by testing laboratories.

Significant technical activities during FY81 in this area have been the following:

(1) Environmentally sensitive fracture is a failure mechanism that critically affects the economic and safe use of alloys in practically every industrial and Government enterprise. Work in this crucial area, on stress-corrosion cracking and hydrogen-embrittlement, has in the main continued to focus on the high purity Al-Zn-Mg alloy and alpha brass and has emphasized mechanistic issues. In the Al alloy, which forms the basis of the high strength aerospace alloys, the role of hydrogen in the stress-corrosion process remains the key question. To investigate this, a comparison was made of conventional stress-corrosion cracking in aqueous sodium chloride and slow crack growth induced by cathodic polarization in dilute hydrochloric acid during stressing, the latter being considered to result from hydrogen-embrittlement. Identical specimens were tested under a constant tensile load with small load pulses periodically applied. Failure is intergranular in both cases, and both fracture surfaces exhibit crack-front markings caused by the load-pulsing technique (see last year's Annual Report). The presence of the markings indicates that crack propagation involves discontinuous brittle fracture. This finding is significant in that it indicates that hydrogen probably plays a key role in the fracture mechanism. Preliminary measurements of the spacings between these markings demonstrated that a plateau velocity exists, corresponding to stress-independent regions of the V-K curves, and that this velocity is approximately 10^{-5} cm/s in both cases. A detailed scanning electron microscope (SEM) study of a large number of specimens was initiated to determine the reproducibility of the method and to obtain precise velocity values. In the next year, the load-pulsing technique will be used to investigate the effects of temperature, environmental conditions, and alloy heat treatment on the plateau velocity. In addition to providing a convenient method for determining crack velocities, the technique provides information on a more microscopic scale than conventional methods. For example, studies of crack-front markings on different intergranular facets in the same specimen should establish whether the crack velocity is significantly influenced by grain-boundary misorientation. Crack growth in the Al alloy was also monitored by the acoustic-emission method. The signals under both test conditions were closely similar, but both were obscured by emissions due to hydrogen evolution. Attempts were made to distinguish the latter from the signals emitted by crack propagation itself.

Studies of the alpha-brasses are relevant to practical failures in condenser tubes. Our previous studies have established that transgranular stress-corrosion cracking in ammoniacal solutions occurs by discontinuous cleavage on (110) planes, the crack advancing typically 5 mm every 20 s. Effort is now being focused on the mechanism of embrittlement. Because of the kinetics, hydrogen was an obvious suspect, but work during the past year has ruled out this possibility. First, attempts to induce transgranular cracking by cathodically charging stressed specimens proved totally unsuccessful. Second, theoretical analysis of the potential and pH values within the stress-corrosion crack demonstrated that hydrogen evolution is not possible. Work was started to investigate an alternative possibility, that vacancy injection at the crack tip due to selective dissolution of zinc can initiate cleavage, possibly by vacancy-dislocation interaction. Attempts are now in progress to produce (110) cleavage by simulating the crack-tip conditions in purely mechanical tests. Specifically, severely cold worked monocrystals of Cu-25Zn are being strained at a low strain rate ($10^{-6} s^{-1}$) at temperatures in the range 25 to 200 °C in an inert environment. The philosophy is that vacancy annihilation during the recovery process is similar to that during stress-corrosion cracking;

the slow strain rate simulates creep at the tip of the stress-corrosion crack. Experiments are also being carried out on high-purity copper to confirm a recent report that transgranular stress-corrosion cracking can be produced. These experiments have obvious relevance to the preceding considerations of dezincification as the critical unit process.

Finally, a fractographic and metallographic study was made on environmentally-induced fractures in steel tendons used in prestressed concrete. This study was carried out as part of a joint program between the National Bureau of Standards and the Laboratorio Central de Ensayo de Materials de Construccione of Madrid, Spain. The steels used in this application are essentially of eutectoid composition and have been patented, i.e., rapidly cooled from the austenitizing temperature to produce fine pearlite, severely cold drawn, and given a low-temperature stress relieving anneal. The resulting highly directional pearlitic structure gives a good combination of strength and toughness, but these steels are known to undergo delayed failure when they are stressed in tension in aqueous media. These failures are generally considered to be due to hydrogen absorption.

The present studies confirm the high susceptibility of pearlitic steels to hydrogen embrittlement. Cleavage cracks were observed to form parallel to the tensile axis, clearly being produced by extremely small normal stresses. However, the highly directional nature of the microstructure makes propagation of these cracks difficult in the transverse plane, causing a partially ductile overall failure in the slow strain rate tests. It seems unlikely that such delayed failures would occur under constant deflection, since such conditions would not be expected to supply the large stresses necessary to produce the ductile component of the fractures studied in the present work.

(2) Improvement in coating techniques for corrosion protection requires better knowledge of corrosion processes under s datings. Progress has been made using a new ellipsometric electrochemical technique developed by NBS which allows, for the first time, the possibility to carry out in situ studies of corrosion processes under organic coatings. This work, partially supported by the Office of Naval Research, seeks to provide new insights into corrosion mechanisms under paints. Such ellipsometric-electrochemical investigations on iron protected by an organic coating have been supplemented in the past year with microanalytical studies of the subcoating microenvironment. Accumulations of chloride ions, three to four times that contained in the bulk immersion medium, have been measured at the coating-metal interface of corroding-coated iron specimens. This phenomenon appears to result from migration of ionic species through the coatings to preserve electroneutrality. A similar mechanism for chloride ion enrichment is thought to prevail in pit and crevice corrosion. The superimposed processes of surface roughening and oxide film thickening which are observed ellipsometrically have been interpreted in terms of the chemistry of iron in very highly alkaline (pH $\sim$ 15) media.

The mechanisms by which the coating-to-substrate bonds fail are poorly understood. One proposed mechanism (see figure 1) states that changes in the nature of the metal surface "oxide" film to which the coating is bonded can result in bond fracture. Recent studies of air-formed surface "oxide" films performed with a newly automated ellipsometer indicate that this surface

layer exhibits very diverse properties depending upon its age and the medium to which it has been exposed. These investigations are being pursued in an attempt to learn more about the coating-substrate adhesion loss mechanisms.

(3) Powerful new electrochemical tools exist or are being developed at NBS that promise to provide sharper insights into corrosion processes or to assist in producing new test methods or monitoring techniques. These tools are being developed and employed for the electrochemical characterization of the corrosion properties of many materials. In the past year this work has entailed the examination of the response of an electrode to very low frequency signals as well as the detection of slow random fluctuations of current and potentials (electrochemical noise). Major accomplishments of this work have been the development of improved methodology for impedance measurements on corroding specimens and the unequivocal demonstration that the development of electrochemical noise is associated with the onset of localized, i.e., pitting, corrosion in several alloy systems. The latter provides an important diagnostic tool which can be used to assess the occurrence of pitting conditions, and may thus form the basis of conditioning-monitoring methods to give warning of localized corrosion in structures and process environments. At the laboratory level, noise measurements can now be used with some assurance to assess the effects of environment, alloy structure, and composition on localized corrosion processes.

The long acquisition times needed to do this work, combined with the increasing complexity in the processing of the experimental data made it necessary to implement some method for automatic operation. To answer this need both the measurement system for determining the impedance of electrodes over a frequency range exceeding six orders of magnitude and the system for the detection and analysis of electrochemical noise have been successfully interfaced to a programmable computer for experiment control and data analysis. In the case of impedance measurements, besides the obvious advantages of being able to examine the results a few minutes after the end of the data taking, and the convenience of graphic representation of the results, the program allows manipulation of the data in a way hitherto impossible. First, it is possible to average a number of identical signals, so as to improve the signal-to-noise ratio. Second, a three-point smoothing routine can be applied to the data collected, effectively filtering away unwanted high frequency noise. Finally, the use of the Fast Fourier Transform (FFT) algorithm as the main way to process voltage and current signals in order to obtain amplitude and phase of the electrode impedance allows the use of pulses other than sine waves, with the advantage of obtaining several values of the impedance at different frequencies in a single run.

This improved measurement system is being applied now to look at the impedance changes which occur at the passive-active transition of some iron alloys.

The noise measurement apparatus has also been interfaced to the computer so that the calculations necessary to separate the deterministic response of the electrode to the input signal from the random fluctuations as developed and described in a recently published paper [U. Bertocci, J. Electrochem. Soc., 128, 520 (1981)], can be done rapidly and automatically, considerably

increasing the productivity of the system. Measurements are now being taken on specimens of a nature similar to buried cables to determine if the noise pattern depends significantly and reliably on the corrosive environment.

(4) A major national concern in the quest for the safe and effective use of nuclear energy generating systems has been the development of reliable systems for the storage of nuclear wastes. A key element in achieving this goal is the development of tests that will assure that containers for this waste can withstand degradation processes until safe levels of radioactivity are reached. A new project addressing these concerns under the management of the NBS Office of Nuclear Measurement Technology was started in the past year. Our efforts are concerned with determining the corrosion behavior of metallic containers, overpacks, and sleeves in the environments similar to those in nuclear waste repositories. The project is concerned with the development of a better understanding of corrosion mechanisms, particularly as it applies to long-term prediction and accelerated testing, development of stocks of research materials, generation and evaluation of key data, and the assessment of the feasibility of long-term field tests.

Electrochemistry and microanalytical laboratories have been set up to be used in the development of an understanding of corrosion mechanisms leading to test methods for assessing localized corrosion susceptibility. The two major pieces of equipment now in place use a spectrophotometer to be used for characterizing localized environments in cracks, pits, and crevices, and a microprocessor-run electrochemical measurement system to be used to carry out polarization, cyclic voltammetric, repassivation kinetics, and other electrochemical studies. Analytical work is under way on the localized environments that develop in a number of simulated ground water formulations. Polarization and repassivation studies have been started for 304 stainless steel in a ground water environment. As an adjunct to these experiments, a theoretical study on the thermodynamic stability of titanium (a leading candidate canister material) in natural environments at various temperatures up to 300 °C is under investigation. The system of Ti-H_2O-Cl was studied first. The approach chosen was the evaluation of electrochemical potentials of titanium in its reactions with water and chlorine and their ionic species at different temperatures and at various pH's, the so-called "Pourbaix Diagram." The chemical stability of titanium can be assessed from such diagrams. The process of evaluation requires a knowledge of the chemistry and chemical equilibria of titanium reactions. However, the information on the required knowledge in the literature is limited, especially for those at higher temperature. To complete the process, it is necessary to limit the study to those compounds that are known to exist and to estimate those thermodynamic data that are lacking at high temperature by following the method of Latimer for estimating ionic entropies and the correspondence principle of Criss and Cobble which relates ionic heat capacities and entropies. The process of estimation of thermodynamic data for those pertinent compounds is in progress.

A bibliography on the corrosion of canister materials in underground environments and a review of canister degradation mechanisms were completed.

(5) The ever-increasing use of buried electric power cables has been plagued by unexpected corrosion problems. Such problems require measurement techniques that allow power company personnel to detect and measure the corro-

sion of cables without excavation. The Electric Power Research Institute (EPRI) has asked NBS to develop such in situ measurement techniques. The latest studies on this EPRI project on techniques to measure the corrosion of concentric neutrals on electric cable indicate that an alternating current to ground of 0.1 mA/cm^2 on the copper concentric neutral (CCN) has no appreciable effect on the corrosion rate measured as compared to a similar CCN without an imposed alternating current. Earlier data taken on other cables in the ground revealed that a higher alternating current to ground (0.7 mA/cm^2) increased the corrosion rate of the CCN by a factor of ten. These latest data are of significance since a study at Georgia Tech indicates that the maximum alternating current to ground expected on an operating cable is less than 0.1 mA/cm^2. In addition, since it is essential that we know the area of the CCN being polarized during the corrosion rate measurement so that corrosion rate per unit area can be calculated, work during the past year has been directed at making such a determination. This area was determined by measuring the change in potential over the length of the cable. The results indicate that this area is a function of the counter electrode distance and the amount of polarizing current applied.

To check the reliability of the polarization techniques developed, measurements were made on operating systems through the cooperation of the Baltimore Gas and Electric Company. Four different sites containing cable in service have been chosen for such a study. Two of these sites are believed to be free of corrosion and two are suspected of having active corrosion. Corrosion measurements have been made at all four sites using the techniques developed at our NBS test site. Current distribution measurements were also made. These sites will ultimately be excavated for verification of our electrochemical measurements.

The development of a microprocessor-run system to enable the making of these measurements by power company personnel is virtually complete. Automation of the corrosion test site located on NBS grounds has progressed to the point of now having a mobile laboratory from where measurements are made. Solid, permanently located $Cu/CuSO_4$ reference electrodes have been installed and wired to the mobile lab. Similarly, counter electrodes are permanently located at the site. Though measurements are still being made manually, interfacing equipment is being assembled which will allow automatic retrieval of data.

Another technique being explored for application to the detection of underground CCN corrosion is corrosion noise measurement. Noise measurements on buried cables under field conditions were made during the past year. Although the instrumentation employed in the field is less sophisticated than that used in the laboratory, limiting by the observations to fluctuations in the electrode potential, the use of a two-channel spectrum analyzer, with capability to measure the cross-power spectrum, has enabled us to take some preliminary readings which seem to indicate that the noise signals observed in the frequency range of a few Hz originate from specific portions of the cable. Although these results are insufficient to show that noise measurements can be successfully employed to detect localized corrosion in the field, they at least do not preclude this possibility.

(6) The corrosion of reinforcement bars in concrete bridge decks caused by the use of deiceing salts has been estimated by the Environmental Protection

Agency to cost the economy more than $200M annually. Efforts to control this corrosion of steel in chloride contaminated concrete using new protection techniques being developed by Government and industry have been hampered by the lack of a nondestructive method for measuring the corrosion rate of steel in concrete. This measurement of corrosion would allow an evaluation of the effectiveness of the various protection systems. During the past year considerable progress was made on a project for the Federal Highway Administration that seeks to develop a technique for measuring the corrosion of steel in concrete.

A major aspect of this effort has been the characterization of the distribution of current over the steel during polarization measurements. The data indicate that the extent of distribution is controlled by the distance of the counter electrode from the steel being polarized and the amount of current applied. The resistivity of the concrete does not appear to affect the distribution of current significantly. The corrosion measurements using these current distribution results and utilizing the Stern-Geary technique have revealed that the rate of corrosion is controlled by the resistivity of the concrete for resistivities over $\sim$ 10 kΩ-cm. In this state the concrete is relatively dry and oxygen is available for the corrosion reaction. With higher moisture content, which results in a concrete resistivity below 10 kΩ-cm, oxygen diffusion is reduced and controls the rate of reaction. Some of these measurements hitherto carried out on concrete slabs in the laboratory have now been made successfully on bridge decks. Also, the development of a microprocessor system enabling the making of corrosion rate measurements is near completion.

(7) Two joint research efforts initiated in FY80 with other Divisions in the Center for Materials Science have been continued. Both of these projects have as their aim the development of a better understanding of how alloy composition and structure affect the passive layers that control corrosion processes. The first is in collaboration with Dr. D. M. Sanders of the Inorganic Glass Group. It is concerned with determining the role played by alloying elements in influencing the properties, especially structure, of passive films. The work uses the new apparatus built by Dr. Sanders and his colleagues that is capable of producing synthetic oxide films of different compositions and being capable of in situ analysis of such films using four different surface analytical tools. A number of electrochemical methods for evaluating the ability of passive films to resist breakdown have been evaluated. The second research program initiated is in collaboration with Dr. M. Kuriyama and Dr. G. G. Cohen of the Metallurgy Division. This work is aimed at using synchrotron radiation to study passive films on metal surfaces. Measurements have been started to study oxide films on copper, iron, and chromium using EXAFS. It has been shown that it is possible to obtain spectra for thin oxide films on copper using a rotating anode x-ray source.

Evaluation of Corrosion Resistance of Materials. This area has as its objective the production of new corrosion resistance data of materials (primarily metals) in environments of practical importance. As a consequence of pursuing this objective, test methods are sometimes developed or those developed in the previously described area are adapted.

Significant technical activities during FY81 in the evaluation of the corrosion resistance of materials have been the following:

(1) A program for the assessment of the suitability of various metals and metal-ceramic combinations to serve in downstream components of a combined MHD-steam plant generator continued this year under the sponsorship of the Department of Energy (DOE). Selected specimens were exposed to fuel rich and oxygen rich metal salt seeded hot gas streams which reproduce some of the characteristics of the harsh environment expected to exist downstream in the heat exchange region of the steam bottoming plant.

Exposure tests were conducted in a simple vertical cylindrical burner rig fueled by an oxygen propane torch. Tubular specimens of boiler pressure tubing steel, ASTM A213-T22, AISI 1015 steel, and AISI 1015 steel arc plasma sprayed with NiCrArY, $MgAl_2O_4$, and $ZrO_6(M_8O)$ were subjected to oxygen rich and fuel rich hot gas streams seeded with K_2SO_4. Specimen wall temperature in the mid-hot gas stream position was maintained at either 700 °C, 500 °C, or 590 °C by internal air cooling. Gas stream temperature in the same vicinity was fixed at approximately 1300 °C. After exposure, metallographically prepared sections of the tubing were analyzed by optical, SEM, and EDX techniques for signs of incipient or gross corrosion.

During exposure, generally, a relatively heavy salt deposit descended to a drip zone of greater thickness at the tube sides. The cinder surface of the tube was coated with a powdery fume deposit. With respect to the ASTM A213-T22 steel, the variances in corrosion due to oxygen concentration are minimal. In both cases, fuel rich and oxygen rich K_2SO_4 seeded hot gas streams, corrosion appeared to occur readily. Ion migration as detailed by EDX analysis shows a relatively high concentration of chromium with the ion at the metal-corrosion band interface with traces of potassium and sulfur. Moving outward through the corrosion band the concentration of chromium diminishes rapidly with a simultaneously increasing concentration of potassium and sulfur. Iron is found beyond the corrosion band-salt deposit interface well into the salt coating. One concludes that this metal would probably not survive in the anticipated environment.

Studies of AISI 1015 mild steel coated arc plasma spraying were started. Such specimens in some cases showed promising corrosion resistance. The NiCrAlY coated steel showed only minor attack, and that at the drip zone, in tests conducted thus far. The bonding between the substrate 1015 steel and the arc plasma sprayed NiCrAlY coating is very good with no evidence of separation due to thermal shock or differential heating.

Coatings of $MgAl_2O_4$ and $ZrO_6(MgO)$ on AISI 1015 mild steel showed no attack from exposure but showed evidence of separation within the coating though not necessarily at the metal-ceramic interface. There were also some instances of fissuring normal to the surface, penetrating the full thickness of the coating. Failures of this type could prove to be catastrophic and must be considered in the evaluation of the material. Further testing of these materials is anticipated.

(2) One of the most extensive studies of the corrosion of piling driven into soils was started by NBS around 1960 under the sponsorship of the American Iron and Steel Institute (AISI). This study was extended, in 1967, to include

an investigation of the effectiveness of corrosion protection of steel piling in sea water by a variety of systems and methods for evaluating the degree of protection with time. These systems consist of metallic and nonmetallic coatings, cathodic protection, and combinations of these systems including bare piles for use as controls. The degree of protection afforded by these systems was measured annually using electrochemical methods in conjunction with visual and photographic records. During the summer of 1980 these piling specimens were removed from the sea water test site and brought to NBS for evaluation of the effectiveness of protection and corrosion deterioration. The taking of data needed for this evaluation was completed during FY81 and will be compared to the electrochemical data taken during exposure. The data thus obtained will be analyzed and a final report which will mark the end of this fourteen-year effort will be written in FY82. Also in FY82 a study of the corrosion of piling driven into landfills will be initiated under AISI sponsorship.

(3) An increase in underground telephone cable installation by the telephone industry throughout the United States has created a demand for comprehensive and reliable information with respect to the corrosion of shielding materials. In order to obtain such corrosion data on both currently accepted and proposed experimental cable systems, the National Bureau of Standards and the Rural Electrification Administration initiated a long-term underground corrosion program. The program was initiated in 1968 with the burial of thirty-one cable systems in selected soil environments. A progress report (NBSIR 81-2243) has now been published describing the performance of various cable systems after exposure for up to six years in different soil environments. Fifty-two different shielding systems (using metal or plastic coated metals) were investigated, some under very adverse conditions. The data show that of the cable specimens buried for up to six years, few were resistant to corrosion in all of the soils in which they were exposed. This year cable specimens were removed from five of the six test sites and are now undergoing evaluation.

(4) A study is underway on the corrosion of metals and alloys used or under consideration for use in waste-to-energy systems supported by DOE, DOD, and the NBS Office of Recycled Materials. This study is directed toward corrosion problems that may exist in incinerator systems where refuse-derived fuels are manufactured. NBS personnel have begun a study of the problem. A corrosion probe has been designed and constructed for insertion into the fire box of the incinerator near the boiler tubes. This probe is made of the alloys whose corrosion will be studied. The first installation was made in the NASA Langley refuse fired incinerator in September 1981.

A literature search on the subject of corrosion in incinerators has been completed and will serve as an aid in defining the areas where more information is needed.

Electrodeposition. Electrodeposition is an important metals processing technology that produces novel, economical, and energy efficient materials and coatings. Improvement of coatings to enhance the corrosion and wear resistance of alloys is a major element in strategies to reduce dependence of U.S. industry on critical materials such as chromium. This area seeks to develop new understanding of the properties and structures of electrodeposits and electrodeposition processes, to improve current electrodeposition technology, to produce and

develop new SRM's that are necessary for the measurement technology used by the plating industry and to devise new SRM's, requiring electrodeposition for their fabrication, for use in nondestructive evaluation techniques.

Significant technical activities during FY81 in this area have been the following:

(1) A new three-year project on plating onto anodized aluminum was initiated under the joint sponsorship of the Aluminum Association and the American Electroplaters Society. Plating on aluminum is important in reducing the weight of automobiles to conserve fuel by the use wear reducing electrodeposited coatings of tin on the piston walls of aluminum engines. The purpose of this program is the elimination of dangerous cyanide electrolytes which are used in other aluminum plating technologies and the reduction of processing costs. The electrolytes used in the anodized processes are mainly dilute solutions of inexpensive mineral acids. Noteworthy accomplishments during the past year include the following:

a. Scanning electron micrographs of adhesion failure specimens show conclusively that poor adhesion is directly related to the strength of the oxide film formed during anodizing pretreatments. Experiments with various electrolytes indicate that, for a given alloy, the strength of the anodic film is related to the pore diameter. The incorporation of the anodizing acid's anion does not significantly influence the anodic film strength when compared to the influence of the film's pore diameter. However, when examining electrodeposit adhesion for a variety of aluminum alloys, anodic film composition, not film structure, becomes the major factor.

b. In attempting to modify the composition of the anodic films metallic salts were added to the anodizing electrolyte. As the concentration of metallic salts increased it became more difficult to develop an oxide film suitable for subsequent electrodeposition. Modification of the anodizing parameters (e.g., temperature, pH, etc.) made it possible to follow the anodizing treatment with a plating treatment merely by reversing the polarity of the current. Results demonstrated that electrolytes with iron and iron-nickel additions could be successfully deposited upon following the anodic treatment and produce moderate adhesion. The adhesion achieved was greater than that achieved without the metallic salt additions demonstrating the importance of the composition of the anodic film.

(2) As imported raw materials become scarce the importance of high performance coatings, not only to electroplaters, but more importantly to American industry becomes important. Electrodeposition of these alloys not only provides the obvious benefit of a cheap substrate, with high performance surface properties, but also, perhaps just as importantly, is a "room temperature" technology. The substrate temperature, therefore, is not affected unlike some related technologies. In addition to this advantage complex geometries are easily coated. A new project in cooperation with the American Electroplaters Society seeks to advance this new processing technology by developing the pulsed electrodeposition of such heat and corrosion resistant alloy coatings was initiated. The focus of this project is on the deposition of Fe-Ni-Cr alloys from aqueous electrolytes. Preliminary experiments in the deposition of Ni-Cr alloys using pulsed electrodeposition have demonstrated the feasibility of the approach used in this new project.

(3) A project on the electrodeposition of glassy alloys has been underway for two years and deals with the pulsed electrodeposition of nickel phosphorus alloys. The results of this program show that electrodeposited nickel phosphorus is at least bimorphous and certain nickel phosphorus alloys exhibit exceptional wear resistance. The bimorphous nature of these alloys was investigated using nuclear magnetic resonance techniques (with L. H. Bennett of Division 564). These results are summarized in figure 2. This finding that two amorphous structures co-exist refutes the predictions of the Free Volume Theory. The wear performance of these alloys was determined by dry sliding ring on block tests (with A. W. Ruff of Division 564). The results indicate that the heat treated alloys have markedly lower (an order of magnitude less) wear rate and higher hardness than the as plated alloys.

(4) A new project is being initiated in cooperation with the NBS Office of Standard Reference Materials for the fabrication of microhardness standards using electrodeposition technology. The main advantage of the use of electrodeposited materials is that the microstructure of the coating can be controlled on a scale small compared to the dimensions of the microhardness indenter. This is extremely difficult and costly to accomplish using other processing technologies involving solidification from the melt. Some standards have been electroformed and shown to be far superior, in hardness uniformity, to the best commercial standards available.

(5) Answering the need of industry for test blocks to check the sensitivity of liquid dye penetrants and of dye penetrant systems for the detection of cracks in structures that can lead to their failure, a new penetrant test block SRM was developed. This development reached a point in the past year where 100 test blocks were produced and delivered to OSRM (see figure 3). To make these test blocks, alternate layers of nickel and copper and electrodeposited on a nickel sheet so that a cross section of the laminate electrodeposit shows thin copper lines between bonds of nickel. The copper is then partially dissolved leaving deep cracks. The test blocks to be used as a Standard Reference Material (SRM) each contain four cracks with nominal crack widths of 0.2, 0.6, 1.0, and 2.0 μm.

(6) A system for the automation of standard thickness SRM production was designed and will be put into operation in October 1981. This system should significantly reduce the production costs of the SRM thickness standards and at the same time improve the SRM quality.

(7) The industries using or producing coated materials such as the electronics, aircraft, and paint industries require a means to calibrate their coating thickness measurement systems. Work continued in the production of coating thickness SRMs that industry requires for the calibration of coating thickness gauges. A single SRM is a metal coupon, 3 x 3 cm or 1.5 x 1.5 cm, one surface of which has an electroplated coating of certified thickness. Most of these are non-magnetic coatings on steel, but also included are nickel, gold, and tin coatings on various metallic substrates. Some 53 different SRMs are made ranging in thickness from 0.7 μm to 2 mm. (Gold coatings are actually certified in units of mass/area, not length.) They are designed for use with either magnetic type or beta backscatter type thickness gauges.

These SRMs are packaged in sets and the SRM catalog lists some 31 different sets. About 5000 individual coating thickness standards were produced during FY80 and about 4700 were produced during FY81.

Chemical and Biodegradation Processes
Subtask 2 of Task 12111

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[1]NBS Guest Worker, February, May, 1981
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The technical activity of this subtask focuses on measurement and mechanistic characterization of chemically and biologically mediated reactions of materials in service environments. These processes affect materials durability, the environmental impact of materials use, and the properties and function of materials such as protective coatings and biocides. The role of organometallic materials and compounds is emphasized because of the increasing use of organometallics in world technology and because of the significance of organic species in degradation, mobilization, and transport of metallic elements.

Specific activities described below under this subtask include development of compound-specific methods for detecting and monitoring key organometallic species down to the ng L^{-1} level and application to current technological problems involving metal-containing materials. Assessment of the stability of certain NBS Standard Reference Materials to biodeterioration is another major current thrust.

Predictive Speciation of Organometallic Materials. Detection and monitoring of organometallic compounds in environmental matrices requires sophisticated measurement methods. High performance liquid chromatography (HPLC) affords a reliable and widely-used method for separation of complex mixtures of molecules and ions under diverse conditions. Coupling to element-specific detectors provides a powerful combination for ultratrace speciation of metal- or metalloid-containing compounds. Such methods are of increasing significance to commercial process monitoring or effluent control strategies especially in the materials protection and energy fields.

Chromatographic methods often rely on comparing chromatography parameters (such as retention time) of unknowns with those of known materials. The power of these methods can be enhanced if chromatographic parameters of candidate materials can be predicted from molecular structure. The quantitative relationship that we demonstrated in FY80 between HPLC behavior and molecular substituent parameters was extended in FY81 from di- and triorganotin compounds to include As as well as Sn, to extend the variety of substituents, and to include both neutral Sn and anionic As(V) species.

Typical chromatograms, obtained using the GFAA-HPLC system, for the separation of organoarsenicals and tetraorganotins are shown in figures 4 and 5, respectively. Molecular substituent values σ^{ϕ} (based on the independently measured

thermodynamic equilibrium of the protolysis of substituted organophosphorous acids) are directly proportional to the logarithm of the empirically determined chromatographic capacity factor, k', for the arsenicals investigated (r = 0.979, figure 6). The analysis of extracts of the proposed oil shale SRM has been performed with the aid of this relationship. Using a similar approach, we have also determined that the ln k' values for the separation of $R_nR'_{4-n}Sn$ species are directly proportional (r = 0.989) to the hydrophobic substituent parameter, π based on the partitioning of a compound between octanol and water. In figure 7, two distinct curves are obtained depending on the presence or the absence of an aryl moiety in the tin compound.

DOE/NBS Workshop on Environmental Speciation and Monitoring Evaluation of Future Requirements for Element-Specific Speciation in Energy-Related Processing. Increased national reliance on alternate sources for extracting fuels and oils either from fossil deposits or from recycled materials directs attention to the processing and environmental hazards shared by both technologies and their common measurement solutions. These joint concerns are raised because it is already clear that fossil sources, such as oil shale or coal, contain significant accumulations of many toxic elements, including arsenic, mercury, selenium, uranium, and cadmium. Dependence upon recycled materials as prospective sources for organic feedstocks requires consideration of the anthropogenic incorporation of the same toxic elements during prior use. Underlying both technologies there exists a major requirement for reliable trace measurement methods and standards.

Assessing or monitoring environmental hazards or impacts of such processes and their effluents is inhibited by many unsolved problems: (1) What are the relationships between the source matrix (coal, shale, sludge, sediment) and the potential for release of toxic metal- or metalloid-containing substances during processing, disposal, or recycling? (2) What are the specific molecular forms of the toxic elements and their dosage effect(s) upon specific or diagnostic organisms? (3) What are (will be) the best means for detecting and quantitating these toxicants in the dynamic process environment as a real-time monitoring control?

At the request of the Office of Health and Environmental Research, Department of Energy, the Division organized a specialist workshop to address these timely questions and appraise the routes by which new relevant research could be most effectively performed. Twenty-four experts gave invited papers at the DOE/NBS Workshop on "Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes," at NBS, Gaithersburg, 18-20 May, 1981. Some 45 additional invited specialists from industry, Government, and academe participated in a full discussion of the issues cited above. The papers and edited discussion are currently in preparation as a Proceedings for publication in the NBS Special Publication series (NBS SP-618). The Workshop was sponsored by DOE and the NBS Office of Recycled Materials.

Speciation of Organotin Volatiles from the Chesapeake Bay. Developing uses of organotins as biocides and antifoulants, together with increasing inputs of tin to the environment from sources such as tin-stabilized polymers, have stimulated work on methods to detect and measure organotin compounds in environmental matrices.

In FY80, we reported preliminary details of a gas chromatographic system (GC), equipped with a flame photometric detector (FPD) for element-selective (tin) detection and a purge and trap (P/T) sampler for water and air analysis. The system has been optimized for speciating volatile organotin compounds in the gas phase and in aqueous systems, such as environmental marine samples and biological fluids (also see work below on NBS Freeze-Dried Urine SRM). A block diagram of the completed P/T-GC-FPD system is shown in figure 8. During FY81 we have applied this system and our methods to analyze solvated non-volatile environmental tin species which can be reduced with sodium borohydride to form the corresponding organostannanes (R_nSnH_{4-n}, R = Me, Et, Bu, and Ph). The volatile stannanes formed during the N_2 purge of the P/T sampler are trapped on a Tenax-GC resin at ambient temperature, and desorbed at elevated temperatures without decomposition. Figure 9A illustrates the chromatographic separation of the methylstannanes formed by hydride reduction of $Me_nSn^{(4-n)+}_{(aq)}$ (n = 1, 2, 3) in the presence of tetramethyltin. Higher resolution for improved identification of peaks has been achieved by the subsequent retrofit of a GC-capillary column and inlet for the GC-FPD (figure 9B), system and is now being adapted to further extend the capabilities of the P/T mode.

Water samples collected from Baltimore Harbor and the Chesapeake Bay for an ONR project concerned with fate and effect of marine organotins were speciated for volatile and non-volatile organotin species using the P/T-GC-FPD method. Two modes of use were designed. Mode I, involving purging of samples directly as received, permitted determination of volatile tin species in the water. In Mode II, sodium borohydride was added to a duplicate or previously purged sample tube and the sample was then analyzed for the non-volatile species. Typical results from the two modes are compared in figure 10 for water samples collected from surface waters of Jones Falls in inner Baltimore Harbor. Inorganic tin was reduced to SnH_4 and volatilized when BH_4^- was added, whereas volatile Me_4Sn is detected in both modes. Tetramethyltin was barely detected in freshly collected (Day 1) bottom water samples, but increased dramatically by Day 7, probably due to microbial production. Clearly, improperly handled or aged samples can give erroneous results for such biologically active materials. Water samples collected at other times as well as other sites likewise gave unexpected results. The most striking results occurred with samples analyzed by Mode I from Jones Falls in Baltimore Harbor in which Me_4Sn (480 ng L^{-1}) was detected along with other tin-containing compounds more volatile than Me_4Sn. These species were subsequently identified as Me_nSnH_{4-n}, n = 2, 3. Methyltin hydrides present (200 to 400 ng L^{-1}) in the Bay water are suspected to be biogenic as well as anthropogenic. GC-MS studies of *in vitro* respirant atmospheres above agar slants of inorganic tin-containing Nelson's medium inoculated with *Pseudomonas 244*, a microorganism isolated from the Chesapeake Bay, have shown evidence of tetramethyltin and methyltin hydrides and production. Whether or not Me_4Sn is a direct product of methylation by *Ps. 244* is yet unknown. It is very likely, however, that Me_4Sn is produced upon decomposition of methylated Sn(IV) species which have possibly undergone bioreduction to form Sn-H bonds.

The occurrence in the environment of tin hydride species, thought to be unstable in aqueous media, is an important finding which has major implications for understanding the environmental chemistry of tin. Available literature does not provide clues to the lifetime of such reactive hydrides in sea water. We are presently measuring protolysis rates of R_3SnH in water and sea water by combinations of FT-NMR and HPLC-GFAA.

Bioaccumulation of Organotin Biocides: In last year's activity summary we reported on accumulation of tributyltin (TBT) cation by tin-resistant bacterial strains isolated from Chesapeake Bay. Microbial uptake is not a metabolically dependent process but a simple adsorption since glucose does not stimulate starved cells to accumulate TBT (figure 8, curves B and C). Metabolically inhibited cells showed similar uptake kinetics. Killed (boiling formaldehyde) cells (figure 11, A and E) accumulated more TBT than live cells, which may indicate metabolic exclusion of TBT occurs in tin resistant cells or simply that additional cell envelope sites were made available for binding TBT as a result of inactivating the cells. The TBT seems to bind mainly at the cell surface since most of it was removed by rinsing cells with a chelating agent (EDTA). The bacterial strains tested accumulated tin (as TBT) to 0.3 to 0.8 percent of their dry weight, corresponding to concentration factors of 356 to 855. Bound TBT did not appear to be tranformed by the tin-resistant bacteria in culture (as reported last year) or by the natural flora of Baltimore Harbor (a tin polluted area) waters and sediments. Time course experiments to resolve this question are in progress. Consequently, the biodegradation of a principal commercial marine antifoulant is as yet unclear.

Size-Exclusion Characterization of Biocidal Organotin Polymers. The U.S. Navy has completed field trials with a variety of organometallic polymers (OMPs) bearing controlled-release organotin moieties which act as highly effective inhibitors of marine fouling. Tests show that biocidal action can be sustained at sea for over five years on ships' hulls. Of critical concern in rapidly developing this technology for military and commercial use will be the needed measurement methodology for correlating detailed molecular properties with field experience, especially relationships between molecular weight range of OMP formulations and the rate of predicted release in the service environment.

We have continued in FY81 to apply combinations of ^{119}Sn FT-NMR and size exclusion chromatography (SEC) coupled with conventional detectors and with our unique graphite furnace atomic absorption detector (GFAA) acting as a tin-selective unit. Aliquots from Navy batch runs of the copolymerization of tributyltin methacrylate (TBTM)-methyl methacrylate (MMA) were preliminarily analyzed by SEC-UV-GFAA as a function of time to provide a kinetic picture of the course of polymerization and the nature of organotin incorporation. Chromatographic results were obtained either from diluted aliquots (including in the aliquot benzene comprising the reaction medium), or aliquots from which benzene was removed by evaporation at 0 °C. The GFAA results of diluted samples showed continuous conversion of TBTM to polymer during the entire course of the reaction.

Interpretation of UV spectra was complicated by the presence of the benzene, but suggested that depletion of low MW chromatographic species (TBTM and MMA) followed the same pseudo-first order kinetics. Inasmuch as the composition of copolymer depends on the rate of addition of each monomer to the growing chain, measurement of changes in MMA is desirable. Removal of interfering benzene from the aliquots resulted in "aging" or polymerization of low MW species.

In further work, we anticipate greater use of conventional differential index of refraction (ΔRI) detectors in tandem with the SEC-GFAA system. These are widely used in the polymer industry and may, as figure 12 suggests, provide a

necessary correlation with the degree of organotin substitution within a critical molecular weight distribution or range. As figure 12 also indicates, the relative responses are not in complete registration in the desirable high MW range (ca. 10^4 to 10^5 daltons), consequently we anticipate incorporating a low-angle laser light scattering (LALLS) detector as well to measure absolute MW. Use of SEC-ΔRI-LALLS in conjunction with ^{119}Sn-NMR to establish the local molecular environment of separated OMP fractions will form the thrust of our future work on a Mil-Spec requested by the Navy.

Examination of the above kinetic run aliquots by FT-NMR showed two peaks in the ^{119}Sn spectra from all the samples (0 to 1440 min). The downfield peak was always about 83 ppm (δ $SnMe_4$ = 0) and was broad (230 Hz); the upfield peak was always about 67 ppm and narrower (75 Hz).

A rough correlation between the HPLC and NMR results was found, in the sense that the early fractions from the kinetic run had most of the Sn in the low MW fraction and also had most of the NMR signal in the high field portion of the spectrum. The peak at 67 ppm is presumably attributable to unreacted TBTM; the reason for its breadth is unresolved but may be due to the existence of Sn in complexes of varying size with the THF solvent. The line width is probably not a molecular correlation time effect, since ^{1}H and ^{13}C NMR spectra of the same material do not show unusually broad lines.

The greater breadth of the downfield peak is believed to arise from the same kind of solvent equilibrium as suggested for TBTM, and in addition to a spread in chemical shifts according to the precise bonding in the polymer chain. There appeared to be a large change of chemical shift with changing ambient temperature.

The ^{119}Sn NMR spectra of TBTM were therefore examined at four temperatures from +10 °C to -20 °C and in $CDCl_3$ or THF as solvent, table 1.

Table 1. Temperature-Solvent Dependence of ^{119}Sn Chemical Shift of TBTM

Solvent	δ at 0 °C (ppm)	Δδ/Δt ppm/°C	linewidth (w) at 0 °C	Δw/Δt
$CDCl_3$	110.90	-0.078	9 Hz	0
THF	65.25	+0.475	60	-2.04 Hz °C

New NBS NMR SRMs. (a) Line-Position SRM. The first NBS SRM for NMR line positions is now in the calibration stage utilizing the new NML high field NMR facility. This standard will be certified for line positions (chemical shifts, δ) in proton and carbon-13 NMR. A mixture of substances has been chosen which gives single lines over the chemical shift range of major interest for both nuclei.

Figure 10 shows both the proton and carbon-13 (proton-decoupled) FT-NMR spectra of the chosen material. This stable sample composition: (1) gives roughly equal intensities in the proton spectrum, and (2) avoids any closely coupled spectra so that the calibration will be independent of field strength. Table 2 gives the composition and approximate chemical shift values for the material to be used.

Table 2. NMR Line Positions and Components

Proton NMR Spectrum			Carbon-13 NMR Spectrum		
Shift, δ	Peak[a]	Compound	Shift, δ	Peak[a]	Compound
0.0 ppm	1	TMS	0.0 ppm	1	TMS
1.406	2	$CH_3COOC(\underline{C}H_3)_3$	22.11	2	$\underline{C}H_3COOC(CH_3)_3$
1.868	2	$\underline{C}H_3COOC(CH_3)_3$	28.05	2	$CH_3COOC(\underline{C}H_3)_3$
3.567	3	p-dioxane	29.62	7	$(\underline{C}D_3)_2CO$
5.293	4	CH_2Cl_2	53.61	4	CH_2Cl_2
7.285	5	benzene	66.99	3	p-dioxane
			79.44	2	$CH_3COO\underline{C}(CH_3)_3$
			96.27	6	CCl_4
			128.36	5	benzene
			169.34	2	$CH_3\underline{C}OOC(CH_3)_3$
			204.37	7	$(CD_3)_2\underline{C}O$

[a]Peak number correlates with figure 13.

(b) T_1 Measurements. A round-robin series of measurements of ^{13}C and ^{1}H T_1 values has begun under the auspices of the Joint Committee on Atomic and Molecular Physical Data (JCAMP), using specially prepared tubes containing material of the same nominal composition as described above. It is known as the result of a survey conducted in 1976 that there is a substantial demand in the NMR community for SRM's of accurately known T_1 values. One of the results of the round-robin measurements will be an indication of the precision and accuracy of calibration that may reasonably be achieved in T_1 measurements. This result in turn will help to decide whether the preparation and calibration of such standards should be undertaken with the NML High Field NMR Facility.

Biodeterioration of SRMs. We are continuing a study to determine the stability of NBS Standard Reference Materials (SRMs) susceptible to biodeterioration. Many of the biological SRMs (e.g., oyster tissue, brewers yeast, orchard leaves) were found to undergo biodeterioration if improperly handled, especially by

exposure to elevated humidity. If handled properly, as set forth in most SRM certificates, we found that biodeterioration should not occur. Freeze-dried urine (SRM 2672), however, is susceptible to biodeterioration if rehydrated with typical non-sterile distilled water which otherwise meets the purity requirements set forth in the current NBS SRM certificate. For example, sterile urine rehydrated with non-sterile samples from NBS and from a university laboratory distilled water (containing up to 1600 viable microbes/mL) supported growth of the indigenous microorganisms. The microorganisms from the university laboratory both bound and volatilized elemental mercury (the only certified element in SRM 2672), causing loss of both quantity and homogeneity of mercury. The volatile mercury was speciated using a GC-AA system previously developed in the Division. Rehydration with sterile water or immediate refrigeration and prompt use will prevent this potential problem.

Speciation of Inorganic and Organotins in Freeze-Dried Urine SRM. Aseptically rehydrated urine, (NBS SRM 2672) analyzed by purge and trap-flame photometric gas chromatography, described above, contained inorganic tin and organotin species as shown in figure 14. This is the first demonstration of speciation of trace organometallic species in a NBS SRM. The results are also of major importance to understanding the transport and fate of tin in a natural biogeochemical cycle which some workers report also includes human metabolism.

In figure 14, the table at the top shows chromatographic retention time (t_R), linear regression values (m = slope, r = correlation coefficient), and estimated tin concentrations of the observed species based on data obtained for authentic tin species added to Chesapeake Bay water. Others have also detected trace quantities of inorganic tin and methyltin species in fresh urine samples, whereas detection of butyltin species in human urine has not been previously reported. This may reflect an anthropogenic source.

Inorganic tin was the dominant form of tin detected in the urine SRM as shown in the table. The concentration of inorganic tin in the urine is reported in the table based on calibration data for Sn(IV), since most data are reported in the literature assuming that tin is in the +4 state. However, tin is most commonly ingested by humans as inorganic Sn^{2+} from sources such as toothpaste (SnF_2) and canned soft drinks ($SnCl_2$). We have recently further demonstrated that SnH_4 can be quantitated in the P/T system by hydride reduction of either or both Sn(IV) and Sn(II) although the calibrations differ considerably. Although the reaction for forming SnH_4 from Sn(II) has been in the literature for years, results are continually reported by others as "Sn(IV)" present in the systems being studied. We regard inorganic Sn(IV) as indistinguishable from Sn(II) when tin is reduced to SnH_4. With this in mind, the concentration of inorganic tin in the urine SRM may be 12.0 ng Sn mL^{-1} if it originated as Sn(II) or as much as 28.1 ng Sn mL^{-1} for Sn(IV).

Organotins in the urine may reflect elimination of ingested organotins or biomethylated inorganic tin. Our speciation techniques for tin in such matrices will be of considerable value in environmental toxicology as well as in future development of species-certified SRMs. We are proposing to extend studies in the latter field during FY82 through cooperation with NBS Office of Standard Reference Materials.

Biodeterioration Studies on CMS STEM Cooling System. Another area of biodeterioration which we have examined during FY81 is a significant clogging problem in the Center for Materials Science's new scanning transmission electron microscope's (STEM) cooling system. This problem has resulted in repeated instrument shutdown and cleaning. The clogging flocs in the system are bacteria which grow on traces of organic matter in the cooling water or possibly on plasticizers in the connecting rubber hoses. The bacteria are predominantly of the genus Zoogloea, a nutritionally versatile slime-forming bacterium which is a well-known floc former in aerobic sewage treatment systems. We determined, in addition to Zoogloea, that a branching, filamentous microorganism, probably an actinomycete, is common in the clogging flocs as is another species, a stalked bacterium probably of the genus Caulobacter.

Preliminary studies with Zoogloea isolates indicate they are very resistant to antibiotics and fairly resistant to mercuric chloride and tributyltin chloride. We are screening other biocides in an attempt to inhibit growth of these hardy microorganisms. Prior to our involvement in this problem, the instrument manufacturer had recommended addition of ethylene glycol as a biocide, apparently unaware that certain bacteria may feed on this compound. The clogging problem intensified after ethylene glycol was added to the cooling system. We are working closely with CMS STEM users to devise a sound cleanup procedure and a reliable preventative maintenance program. Clogging problems in these instruments are widespread at NBS. The microbial involvement in these problems deserves more attention.

a

CATHODIC REGION

$2e + \frac{1}{2}O_2 + H_2O \rightarrow 2OH^-$ (major cathodic reaction)

$Fe + 3OH^- \rightarrow HFeO_2^- + H_2O + 2e$ (minor anodic reaction)

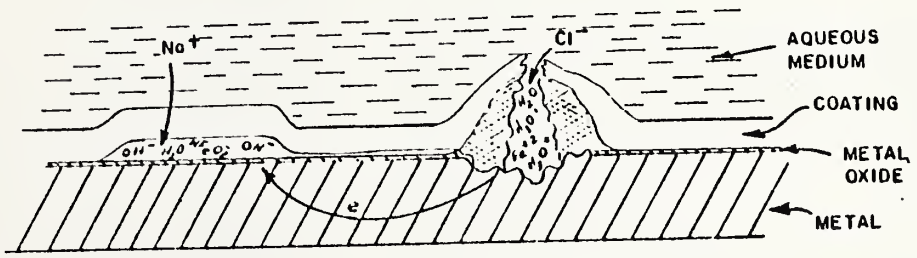
$2HFeO_2^- \rightarrow Fe_2O_3\downarrow + H_2O + 2e$ (precipitation)

ANODIC REGION

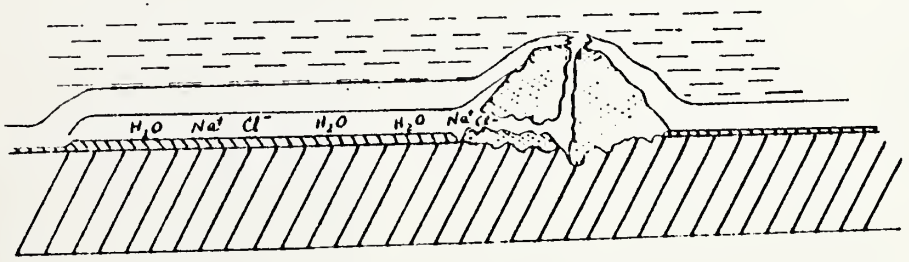
$Fe \rightarrow Fe^{+2} + 2e$ (major anodic reaction)

$Fe^{+2} + 2H_2O \rightarrow Fe(OH)^{+1} + H_3O^+$ (hydrolysis)

b



c



d

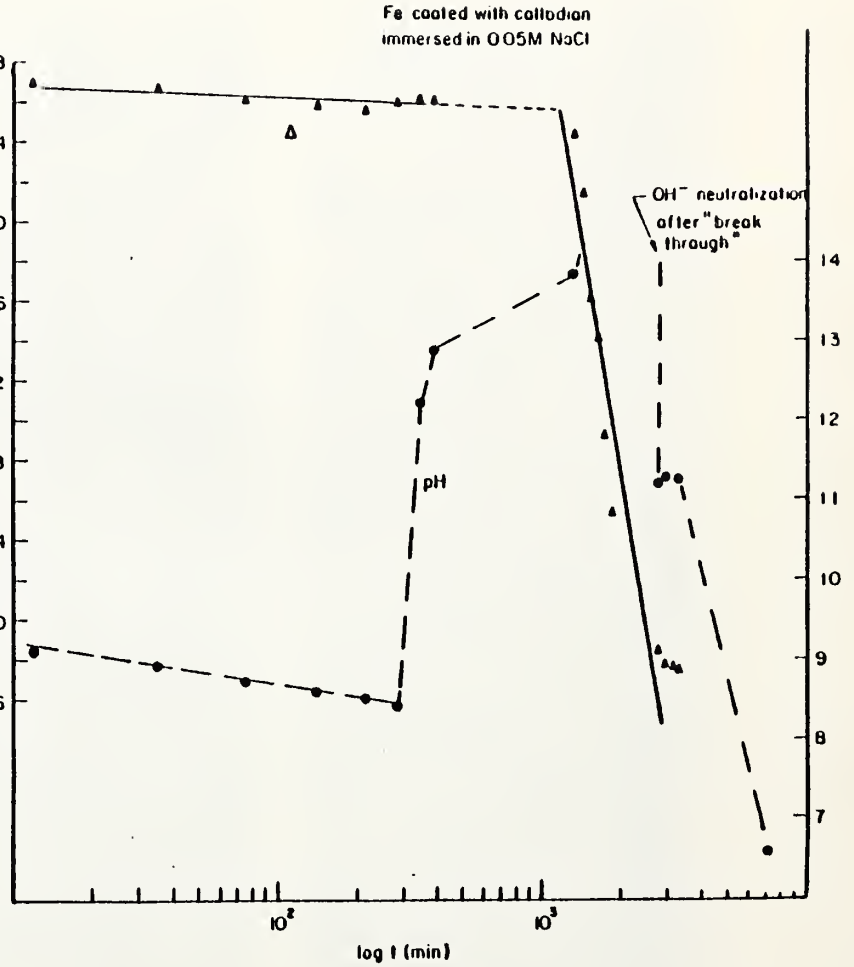


Figure 1.

a. A summary of the equations proposed for subcoating events leading to surface roughening, oxide film thickening and the promotion of Cl^- ion accumulation.

b. Schematic showing Cl^- ion entry into the hollow cone of anodic corrosion products in the presence of a remote cathode.

c. Schematic suggesting one mode of anodic-cathodic "breakthrough."

d. Experimental curve showing change in the ellipsometric parameter Δ (measure of corrosion product film growth and surface roughening) and pH as subcoating process proceeds. Steady decline of pH after 1200 min. indicates a "breakthrough" between anodic and cathodic sites in the vicinity of the subcoating pH probe.

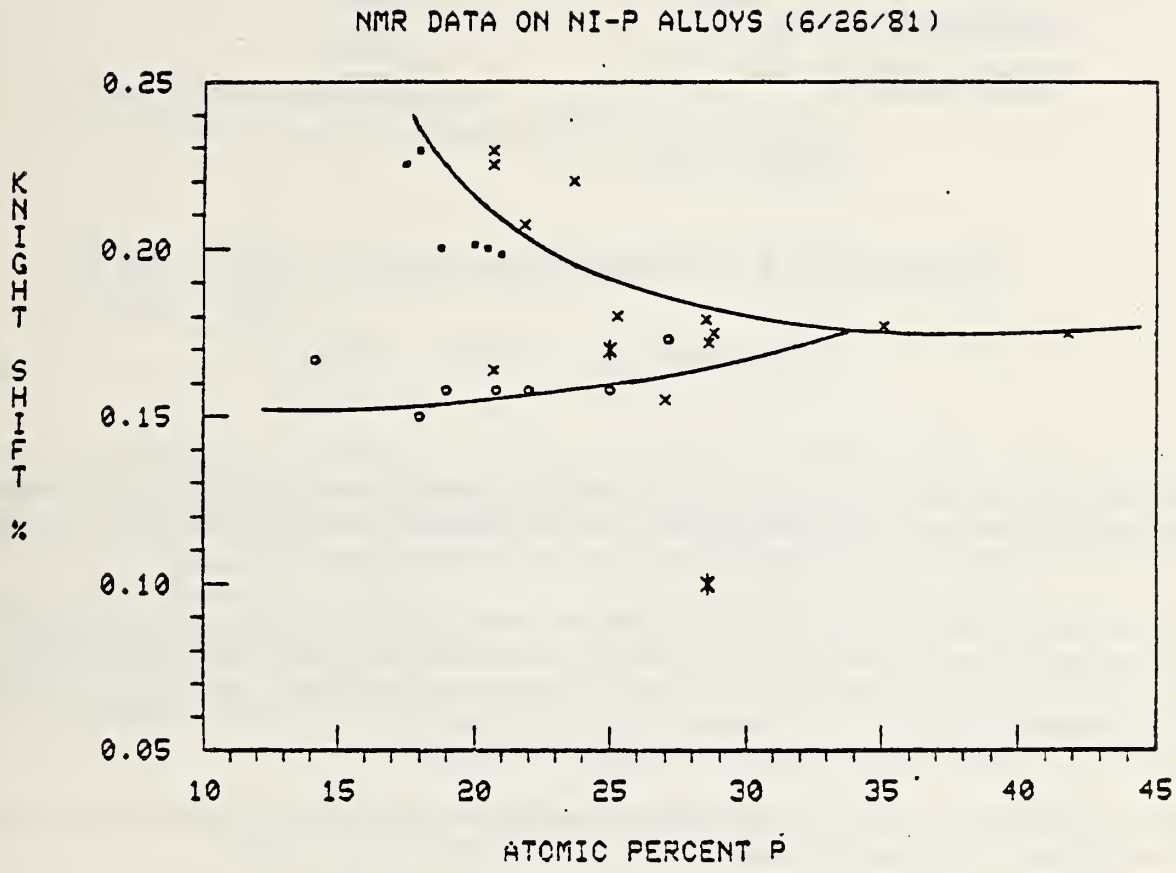


Figure 2. The phosphorus Knight shift as a function of the atomic percent phosphorus. The results show the existence of two amorphous (bimorphous) structures.

NBS Standard Reference Materials

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

Standard Reference Material 1850

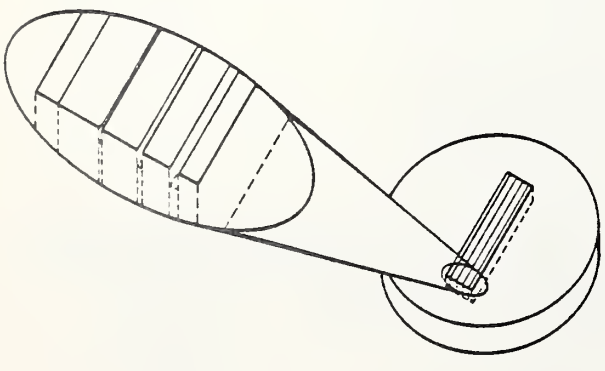
Penetrant Test Block

Winter 1981

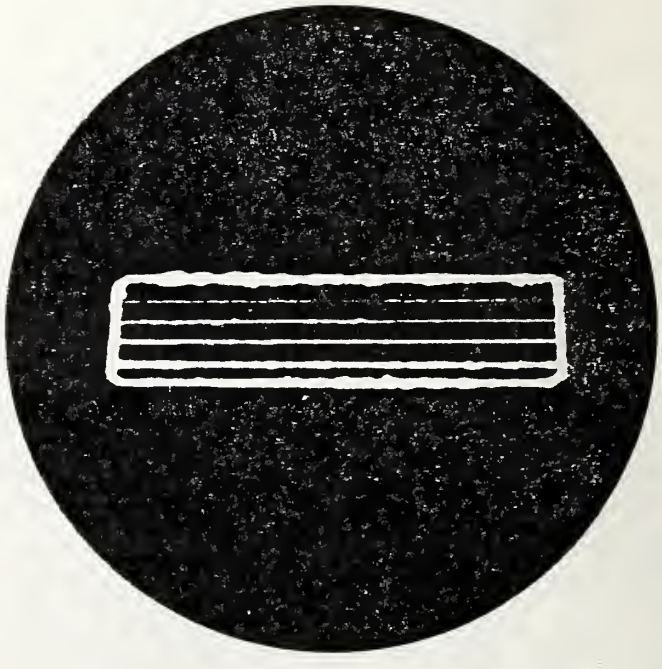
The NBS Office of Standard Reference Materials announces the availability of SRM 1850, a penetrant test block containing uniform "cracks" of known width for checking the sensitivity and performance of surface-defect detecting materials and devices, mainly liquid dye penetrants and dye penetrant systems. The test blocks were developed by the Corrosion and Electrodeposition Group of the Center for Materials Science.

Four cracks approximately 0.2, 0.5, 1 and 2 μm wide are formed in a 1/2 x 2 cm section of an electrodeposited copper-nickel laminate mounted in an epoxy resin disk about 5 cm in diameter and 1 cm thick. The depth of each crack is several times its width—beyond the critical depth for showing dye penetrants. Each crack is measured at the center of the blocks with an accuracy of 50% or 0.1 μm whichever is greater. The test block may be used indenfinitely as it is easily cleaned and corrosion resistant. Further details are furnished with the SRM.

SRM 1850 may be purchased from the Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Washington, D.C. 20234, for $108. (301) 921-2045.



The test block is a cross section of a laminate of electrodeposited nickel and copper - the copper being electroetched to form the cracks.



The four cracks are made visible with a sensitive fluorescent liquid dye penetrant under ultraviolet light. The narrowest crack may not show well in reproduction.

Figure 3. Announcement of availability for purchase of the Penetrant Test Block (SRM 1850).

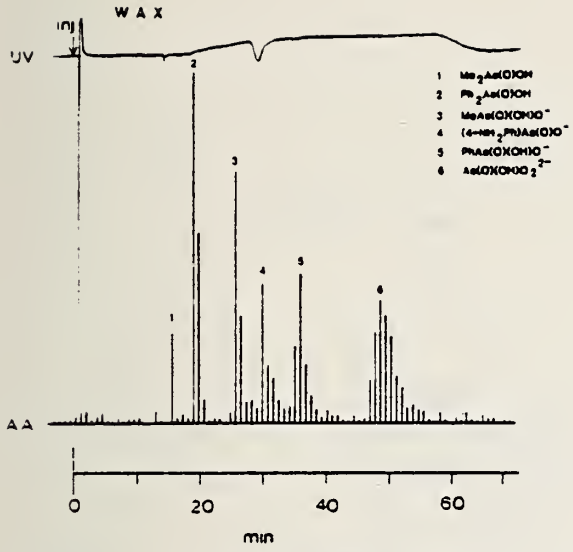


Fig. 4. UV and arsenic-specific AA chromatograms for an aqueous solution containing five organoarsenic acids and arsenate (as numbered) are compared. Complete separations of this and similar mixtures of other arsenicals were effected in comparable analysis times.

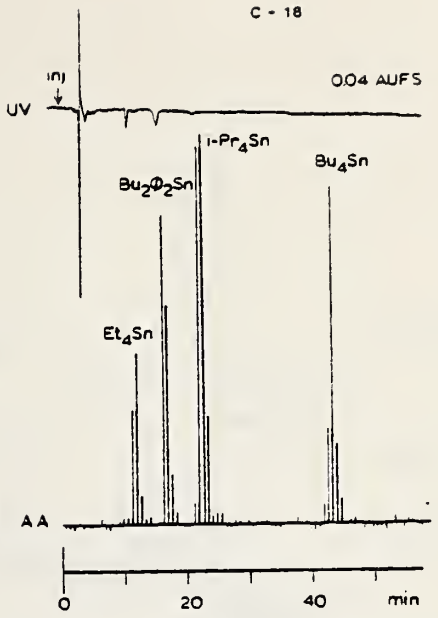


Fig. 5. The separation of four tetraorganotins on an octadecylsilane chemically bonded-phase columns, using methanol: H_2O (93:7 vol_%) at a flow rate of 1.0 mL min^{-1}. ϕ = phenyl or Ph.

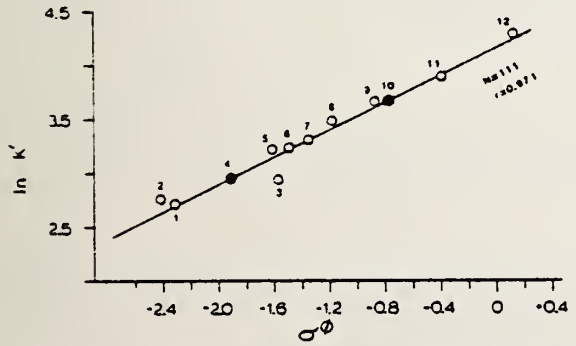


Fig. 6. The linear regression between ln k' and $\Sigma\sigma^{\phi}$ obtained on a weak anion exchange column (WAX) is shown for the following arsenicals: 1, $Me_2As(O)OH$; 2, $Pe_2As(O))_-$; 3, $Ph_2As(O)OH$: 4, $Me_2As(O)O^-$; 5, $BuAs(O)(OH)O^-$; 6, $EtAs(O)(OH)O^-$; 7, $MeAs(O)(OH)O^-$; 8, $(4\text{-}NH_2Ph)As(O)(OH)O^-$; 9, $PhAs(O)(OH)O^-$; 10, $As(O)(OH)_2^-$; 11, $As(O)()H)O_2^{2-}$; 12, $(4\text{-}NO_2Ph)As(O)O_2^{2-}$. The black circles indicate estimated ln k' for alternate choices of protonated or deprotonated arsenic species not acceptable in the fit shown.

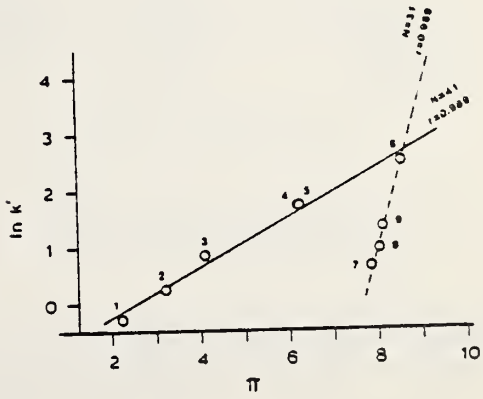


Fig. 7. The linear regression between ln k' and $\Sigma\pi$ on a reversed phase C-18 column is shown for the following organotins: 1, Me_4Sn; 2, Me_2Et_2Sn; 3, Et_4Sn; 4, i-Pr_4Sn; 5, n-Pr_4Sn; 6, Bu_4Sn; 7, Ph_4Sn; 8, Ph_3BuSn; 9, Ph_2Bu_2Sn.

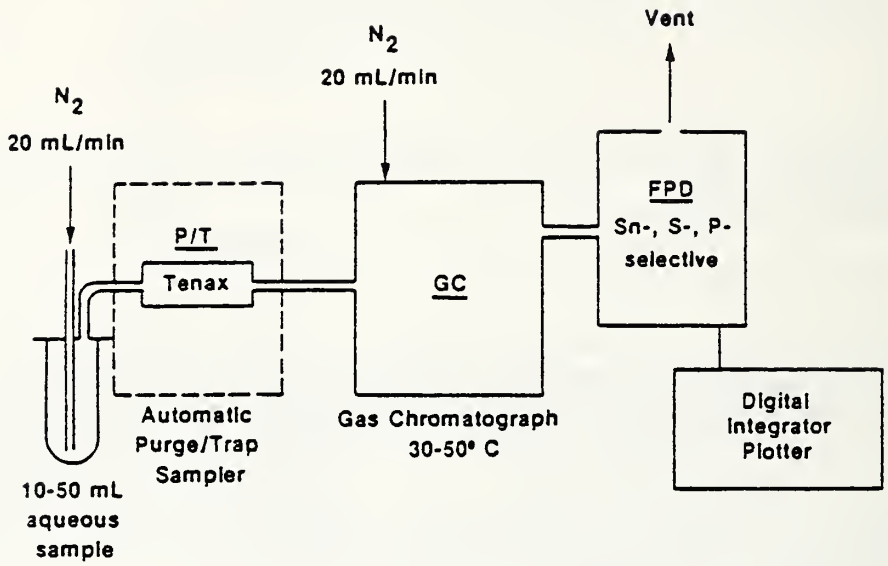


Fig. 8. Block diagram of P/T-GC-FPD system.

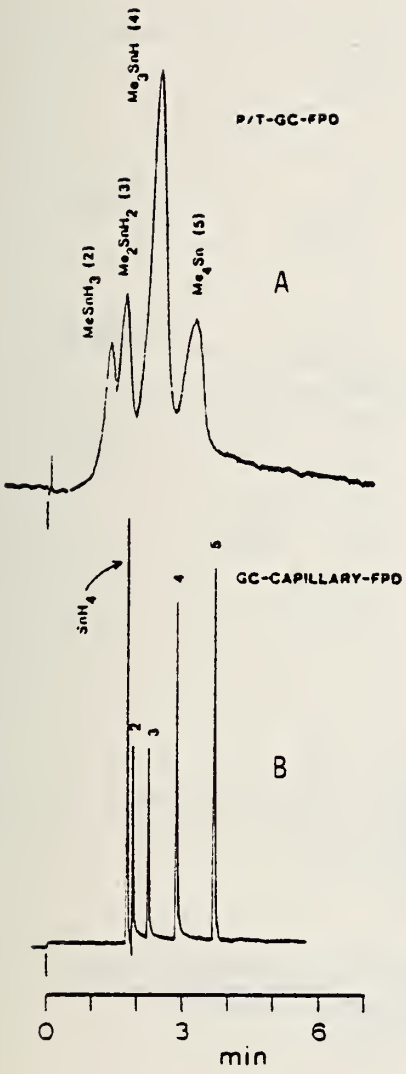


Fig. 9. Gas Chromatographic separation of methylstannanes.

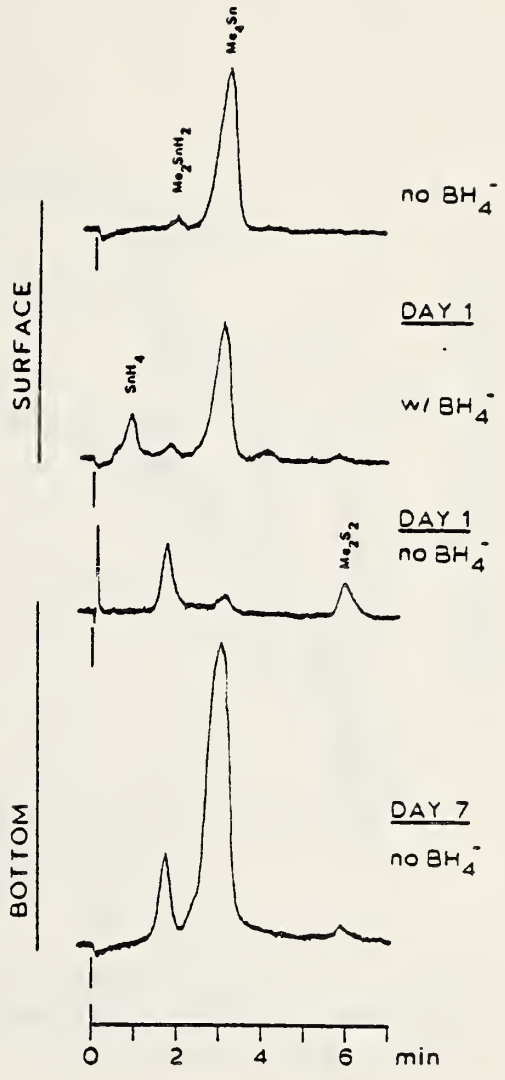


Fig. 10. Chesapeake Bay water samples analyzed by P/T-GC-FPD method using mode I and mode II.

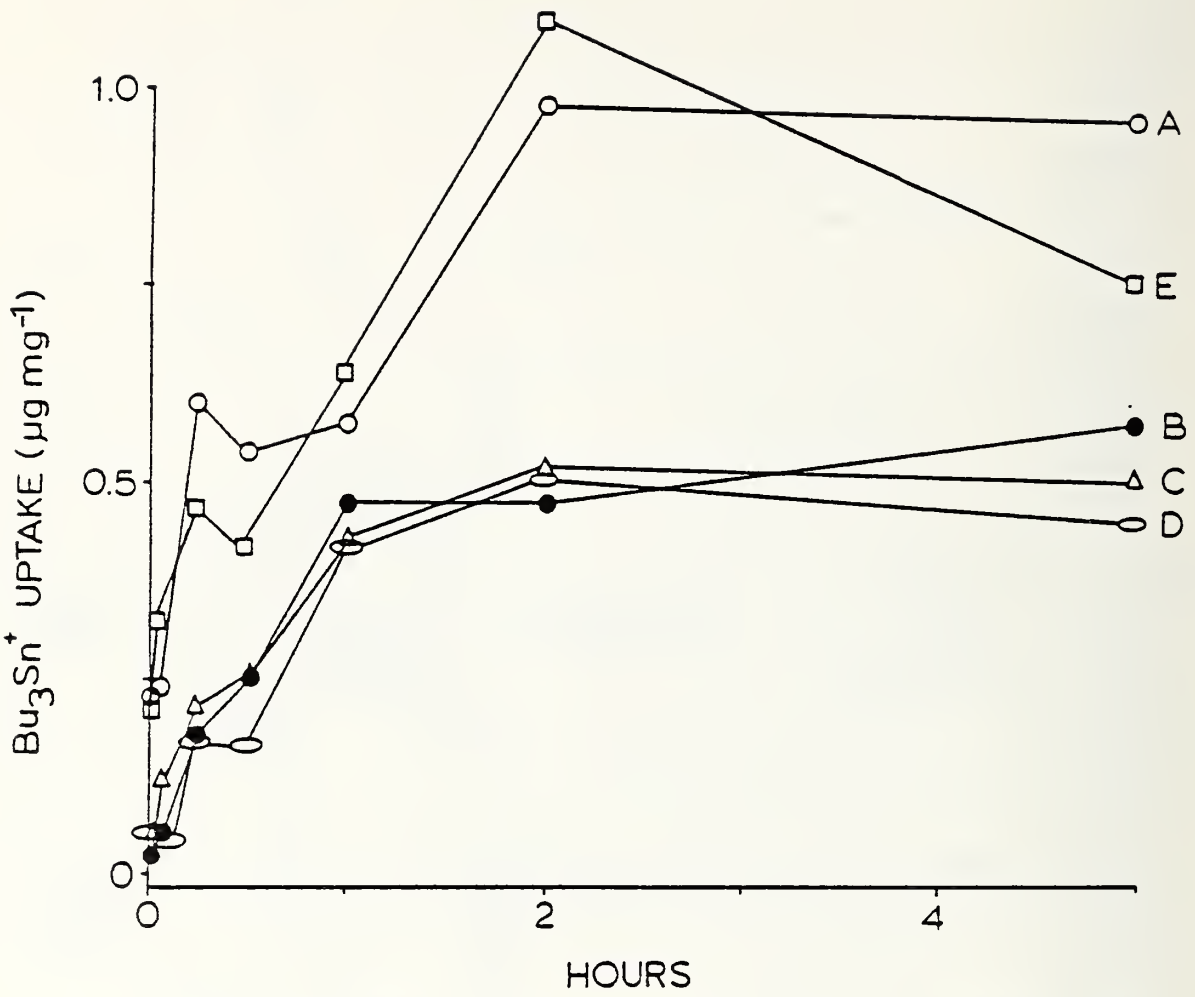


Fig. 11. Tributyltin cation accumulation by starved Pseudomonas 244. A, boiled cells; B, cells--no treatment; C, cells plus glucose; D, cells plus sodium azide; E, cells plus formaldehyde.

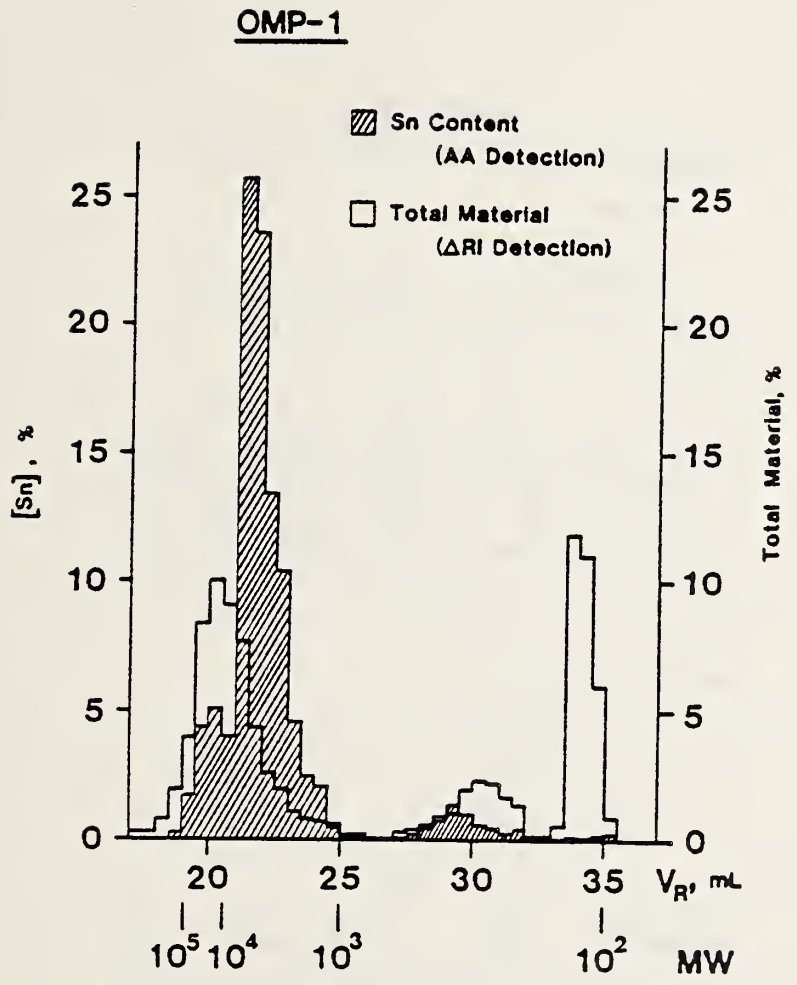


Fig. 12. Correlation between conventional differential index of refraction (ΔRI) and GFAA tin-specific detectors for a Navy OMP formulation.

Fig. 13. FT-NMR spectra of typical SRM tubes. Identities of peaks are enumerated in table 2.

NBS SRM 2672 - Freeze-dried Urine

	$t_R \pm SD$, min	m	r	ng Sn mL^{-1}	
SnH_4	0.94 ± 0.02	617	0.99	28.1	—●—
$MeSnH_3$	1.33 ± 0.03	625	0.93	1.0	--○--
$BuSnH_3$	4.06 ± 0.04	486	0.93	1.5	—▲—

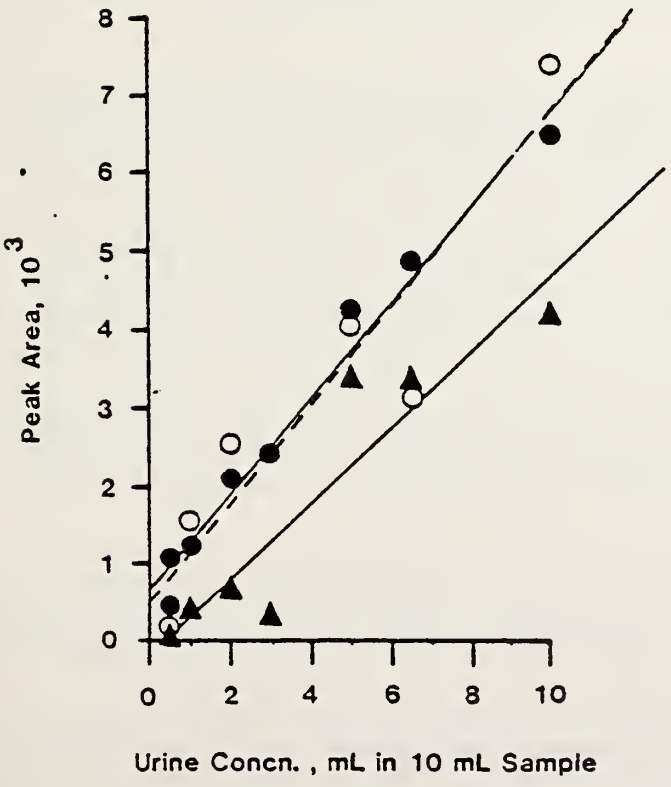


Figure 14. Speciation by P/T-GC-FPD of trace inorganic and organotin species in NBS SRM 2672, Freeze-dried Urine.

HIGH TEMPERATURE MATERIALS STABILITY AND PROCESS CHEMISTRY
Task 12112

The objectives of this task are to develop molecular specific experimental methodology and theoretical modeling tools, and apply them to the determination of basic data and chemical mechanisms for interactions of metals and ceramics with aggressive gaseous high temperature service environments. These methods primarily emphasize the identification of molecular species, together with accurate measurement and model predictions of their concentration, spatial, and temporal distribution in high temperature vapors and gases and in the presence of complex solid or liquid phases. The related in situ measurement problems of temperature and flow (gas phase) are also addressed by this task. For discussion purposes we have separated the principal task into three subtasks, Chemical Vapor Transport in Reactive Atmospheres, Characterization Methodology for High Temperature Gaseous Service Environments, and Thermophysical Properties of Solid and Liquid Tungsten.

The results of this work are required for performance predictions and test method development in new high technology applications (coal-combustion and conversion, advanced propulsion systems) and to support materials processing at high temperatures (chemical vapor deposited coatings, metallurgical and ceramic processing). Principal accomplishments during FY81 include the following:

(1) The operating regime of the transpiration mass spectrometric (TMS) technique was extended to permit partial pressure measurements of high temperature species in corrosive environments at pressures up to 10 atm.

(2) Empirical and theoretical solution activity models were developed for potassium-containing coal slags representative of many coal types. These models can now be used to generate a data base for computer prediction of magnetohydrodynamic (MHD) seed-slag interaction and alkali transport and corrosion in downstream MHD heat-exchanger and other components.

(3) A thermodynamic data base (alkali species activities, Gibbs energies) and computer models were developed, leading to a quantitative molecular description of alkali vapor transport and deposition in glass and slag-combustion systems.

(4) Large literature discrepancies in glass and slag alkali activity data were resolved through identification and characterization of the role of alkali carbonate impurity and water solubility effects on solution thermodynamics.

(5) A novel means of extracting potassium from magnetohydrodynamic (MHD) channel slags and other silicate phases was demonstrated using a salt alkali exchange process. This process could be used to recycle spent seed in MHD generators or for the metallurgical extraction of potassium (and, most likely, rubidium and cesium) from low grade ores.

(6) A laser enhanced ionization (LEI) technique was developed for profiling gas flow velocities, diffusion, and ion-molecule recombination in alkali-laden high temperature gas streams.

(7) A novel laser enhanced ionization technique for monitoring potassium atom concentrations in high temperature gas streams was demonstrated.

Plans for FY82 are: to apply the newly developed TMS capability to determine the mechanism of alkali vapor transport in high pressure Cl and S-containing atmospheres for glass and slag systems typical of coal conversion/ combustion systems; to couple the newly developed laser diagnostic techniques with the high pressure sampling mass spectrometric apparatus for simultaneous optical and mass-spectrometric characterization of high temperature gas streams; to further develop solution activity models for complex silicate melts through a combination of experimental and computer modeling approaches and to apply these models to predictions of alkali vapor transport in coal conversion and combustion systems; and, to further investigate the unusual phenomena of non-equilibrium heterogeneous reactions and H_2O-solubility effects on alkali vapor transport from complex oxide phases. The work of this task is carried out under three subtasks as indicated below.

Chemical Vapor Transport in Reactive Atmospheres
Subtask 1 of Task 12112

J. W. Hastie, D. W. Bonnell, W. S. Horton, E. R. Plante, A. B. Sessoms

This subtask develops and applies new or improved measurement techniques to the molecular-level analysis of vaporization processes for high temperature solids (e.g., ceramics) and melts (e.g., coal slags, glasses and salts) in process atmospheres containing reducing, oxidizing, carbonated, halogenated, sulfated, and hydrous components. These conditions and the data obtained are generic to high temperature process environments, and particularly those where hot corrosion and high temperature oxidation are materials-limiting factors. For example, in the developing technology of pressurized fluidized bed combustion (PFBC), removal of coal and dolomite-derived alkali (Na and K-containing species) impurities to a gas stream concentration level below 0.02 ppm is critical to successful implementation of PFBC. Our participation, at DOE's request, in the DOE-Morgantown Energy Technology Center R&D program on particulate and alkali control in coal combustion process streams, provides for close interaction and technology transfer with Industrial participants, particularly General Electric, Westinghouse, the Electric Power Research Institute, Exxon, and a number of relatively small air pollution technology companies.

In cooperative work with DOE sponsors, the recent measurement focus has been on ceramic, coal slag, and glass systems in atmospheres typical of open cycle coal-fired magnetohydrodynamic (MHD) plasmas, coal gasifiers (CG), and pressurized fluidized bed combustors (PFBC). These extreme conditions have required continued development of the transpiration (TMS) and modulated molecular beam Knudsen effusion (KMS) mass spectrometric techniques. Complementary efforts in data-base (solution activities, species Gibbs energies, ...) acquisition and computer modeling have also become an integral part of this extreme-environment characterization effort during the past year. For most of the coal conversion and combustion systems of interest, the chemical state of Na and K-containing species represents a pervasive theme in our understanding of the high temperature process (e.g., MHD plasma conductivity and seed recovery) and of materials durability problems (e.g., in CG and PFBC). Examples of recent experimental and modeling activities pertinent to these problems are summarized as follows.

Reference State Materials. In order to obtain a definitive experimental/modeling characterization of complex heterogeneous mixtures it is first necessary to have available reliable thermodynamic (Gibbs energies of condensed and vapor species) and mass spectrometric (electron impact fragmentation patterns) data for the single component reference state phases. For the complex systems of current interest, the pertinent reference state materials (solid, liquid, and vapor) are: NaOH, NaCl, Na_2CO_3, Na_2O, Na_2SO_4, and the corresponding potassium analogues. The concept of reference state materials is particularly important to the definition of solution thermodynamic functions such as activities where, for instance, in the case of a potassium silicate slag the K_2O activity (a) is defined by,

$$K_2O\ (slag) = 2K + 1/2\ O_2$$

$$a_{K_2O} = \frac{(PK^2 \cdot PO_2{}^{1/2})\ slag}{(PK^2 \cdot PO2^{1/2})\ pure\ K20\ (1)\ reference\ state}$$

We have obtained the necessary thermodynamic and mass spectrometric data for most of these systems by experiment or by empirical correlation procedures. Previously available thermodynamic data for these systems have, for the most part, been notorious in their lack of reliability and accuracy.

Complex Oxide, Slag, and Glass Systems. New vapor pressure and activity data have been obtained as a function of temperature and condensed phase composition for synthetic slag and silicate glass samples using the TMS and KMS techniques. In addition, a substantial body of similar vaporization data obtained previously (by HTP group) has been analyzed, correlated, and cast in analytical form suitable for computer modeling. These analytical expressions, incorporating alkali vapor pressures and activities, as a function of composition and temperature, can also be used by design engineers for prediction of vapor phase alkali transport and phase stability parameters in coal conversion/combustion, glass melting, and other high temperature operations. A summary of the systems for which such data are now available is given in table 1. Almost no literature data exist for these, or comparably complex, oxide systems.

For the few cases where literature comparisons are possible, serious discrepancies in activity and partial pressure data obtained by various workers are revealed, as shown by the examples in figures 1 and 2. Numerous tests for equilibrium, and accuracy of temperature and partial pressure measurement, as well as comparisons between KMS and TMS-derived data ensure the reliability of the present results. With reference to the data comparison for the binary system in figure 1, the results of Spacil are in error owing to the inherent inaccuracies and assumptions in converting phase diagram data to activities. Similarly, the Charles data are based on a reanalysis of earlier transpiration work in moist atmospheres where assumptions of species identities and distribution, as well as vapor saturation, probably led to large errors. The model curve is a test of the common approximation of assuming ideal mixing of known silicate compounds (e.g., $K_2O{\cdot}SiO_2$ and $K_2O{\cdot}2SiO_2$) where, given the Gibbs energy data, one can calculate activities as shown in figure 1. We have included several common ternary phases in figure 1 to show the sensitivity of activity coefficient data to the choice of phase in modeling. The curve of Spacil is for the high

Table 1

Oxide Systems for Which Vaporization Data Have Been Obtained[a]

System	System
K_2O-SiO_2	Synthetic "Western" MHD Channel Slag:
K_2O-Al_2O_3	K_2O (22.7), Al_2O_3 (24.6), Fe_2O_3 (5.3),
K_2O-ZrO_2	
K_2O-Fe_2O_3	Synthetic "Eastern" MHD Channel Slag:
K_2O-Al_2O_3-SiO_2	K_2O (23.6), Al_2O_3 (25.5), Fe_2O_3 (12.5),
$KAlSiO_4$	CaO (1.8), MgO (0.6), SiO_2 (36.0).
Simplified "Western" Slags:	Illite: K_2O (7.4), Al_2O_3 (26.0),
K_2O-CaO-Al_2O_3-SiO_2;	Fe_2O_3 (4.4), MgO (2.1), SiO_2 (60.2).
Real MHD-Channel Slag (K_1):	Low Melting Synthetic Slag (K2):
K_2O (19.5), Al_2O_3 (12.1),	K_2O (8.7), Al_2O_3 (11.1), Fe_2O_3 (12.0),
Fe_2O_3 (14.3), CaO (3.8),	CaO (13.9), MgO (7.9), SiO_2 (47.3).
MgO (1.0), SiO_2 (46.8),	
Na_2O (0.5).	Glass: Na_2O (17), CaO (12), SiO_2 (71).

[a]Values in parentheses given in wt.%.

sanidine phase assumed to be present in pressurized fluidized bed systems. However, for high K_2O concentrations, kalsilite ($KAlSiO_4$) is the preferred phase. For the glass systems represented in figure 2, the apparent discrepancy between workers, and for different experimental techniques, has been largely resolved through a thermodynamic analysis where the presence of Na_2CO_3 impurity is responsible for the anomalously high sodium partial pressures (e.g., the TMS and Cable data of figure 2). These impurity effects were apparently ignored in previous glass studies (made elsewhere) and, as is evident in figure 2, such effects can lead to serious errors in alkali vapor transport measurements over glass. The KMS (3) data (see figure 2) were obtained for a sample essentially free of Na_2CO_3 impurity and these are the recommended data for a clean soda-lime-silica system.

Alkali Exchange Processes. Preliminary TMS experiments on an MHD channel slag + NaCl mixture indicated effective leaching of potassium from the slag into the molten salt phase by an alkali exchange process:

$$K_2O\ (slag) + NaCl\ (l, g) = Na_2O\ (slag) + KCl\ (l, g).$$

This process has potential as a means of recovering lost MHD seed potassium from the highly bound slag phase. Also, the recent observation of potassium release to the vapor phase in sodium species gettering in PFBC gas stream clean-up tests (P. Mulik, Westinghouse Electric Corporation) can be explained in terms of this process. During the past year, a more detailed thermodynamic analysis of the alkali exchange process was performed using the KMS technique and a lower K_2O-content (8 wt %) slag. The results indicated a virtually complete transfer of potassium from the slag to the salt phase and under solidus conditions. Activities of KCl and NaCl in the solid-solution salt phase were in good agreement with literature data for the binary salt system, indicating thermodynamic equilibrium in the alkali exchange process at temperatures as low as 700 K.

Heterogeneous Systems. Under service conditions, atmospheric components such as H_2O, H_2, and O_2 can be expected to significantly modify alkali vapor transport through mass action effects or by formation of new molecular species. Previously initiated experimental work has continued on heterogeneous systems containing Na and K-benzoate, Na_2SO_4, Na_2CO_3, glass, and slag using the TMS and KMS techniques. Sufficient data have now been obtained to reveal a number of potentially important novel aspects of these heterogeneous processes. First, even though the high temperatures involved (1000 to 2000 K) and the relatively long gas residence times (up to 20 s) would normally ensure attainment of thermodynamic equilibrium, many instances of non-equilibrium behavior were found. Typical examples are given in table 2. Note that certain gas phase processes attain equilibrium but others do not, and likewise with the gas--solid (or liquid) reactions. Further work is in progress to rationalize these observations.

Another unusual, and highly significant, phenomenon was noted in the form of an isothermal partial pressure dependence of atomic potassium on $P(H_2O)^{1/2}$ over real and synthetic slag phases. The most reasonable explanation here relates to the known H_2O solubility in silicate melts. Literature data on H_2O solubility in silicate melts can be interpreted in terms of Si-O bridge forming or breaking processes in the silicate polymer matrix, depending on the degree of basic or acid character in the silicate melt. These structural changes

should also be reflected in the solution activity and hence vaporization properties, as observed. From the data obtained thus far, it is apparent that under the high H_2O pressures characteristic of process atmospheres, the rate of vaporization for alkali metal species could be several orders of magnitude greater than expected owing to this H_2O solubility effect. The rationalization developed to interpret these observations also suggests the possibility of retarded alkali vapor transport, particularly for highly basic systems such as certain nuclear waste glasses. Much of the disparate vapor transport literature data for silicate (slag, glass, etc.) systems may result from effects of this type.

Extension of TMS Technique to 10 atm/Corrosive Atmospheres. The efficiency for high temperature processes of practical concern, such as power plants, turbines, MHD plants, steel making and other metallurgical processes, usually increases with increasing pressure. Many such processes operate at gas pressures in the range 1 to 10 atm and a few (e.g., naphtha reformers and some coal gasifiers) at pressures of 10 to 80 atm. Thermodynamic arguments suggest an increasingly complex chemistry at high gas pressures, e.g., formation of hydroxide and hydrated vapor species in the presence of H_2O. Rate limited processes are also pressure dependent and the somewhat unexpected observation of nonequilibrium reactions (see table 2) indicates the desirability of obtaining data at pressures approaching those of actual process atmospheres. We have therefore extended the operating pressure capability of the TMS technique from one to ten atmospheres. The apparatus has also been upgraded to handle corrosive gas components for analysis of heterogeneous reactions believed to be significant in hot corrosion environments. As a representative case we have selected a soda-lime-silica glass system in a 10 atm gas mixture containing HCl. This system simulates the conditions expected in a pressurized fluidized bed combustor with glass particle trapping and where the possible undesirable introduction of alkali to the gas stream (as NaCl) is of concern. Preliminary data have been obtained indicating that this is indeed a significant process. The ability of the TMS apparatus to function in 10 atm corrosive atmospheres was also established.

Computer Modeling. Reactions between combustion atmospheres and non-ideal solution condensed phases, including slags, glass, and alkali sulfate-hydroxide melts, have been modeled using the SOLGASMIX and NASA-equilibrium computer codes. Our experimental results on species stabilities and solution activities were used to generate the data base for these modeling computations. Several useful approximations were determined for representing slag activity data in analytical form suitable for the computer data base. For instance, it was found that the couples CaO and MgO, and similarly Fe_2O_3 and Al_2O_3 had similar effects on the K_2O activity data in real and synthetic slags containing six oxide phases. Hence these six component systems can be represented, more simply, by a four component system containing SiO_2, Al_2O_3, CaO, and K_2O, as shown in figure 3. This approximation greatly simplifies the modeling problem, as well as allowing for the prediction of alkali activities in actual slags, particularly of the sub-bituminous "Western" type. The availability of accurate activity data for these four component slags also allowed us to evaluate various solution models proposed by others. These comparisons between experimental data and solution model predictions revealed areas where the solution models are in greatest error.

Table 2

Departure from Equilibrium in Reactive Gas Atmospheres

Reaction	Equilibrium Constant Ratio Actual/Apparent	Comments
Non-Equilibrium		
SiO_2(c, illite) + H_2 = SiO + H_2O	350	1750 K, ~ T independent
SiO_2(c, illite) = SiO + ½ O_2	0.03	excess O_2
SiO_2(c, quartz) + H_2 = SiO + H_2O	47	~ T independent
K_2O(c, K_2 slag) + H_2 = 2K + H_2O	49	1650 K
Na_2O(c, glass) + H_2O = 2NaOH	> 10	1400 K
K(g) + ½ H_2O + ¼ O_2 = KOH	32	1794 K
H_2 + ½ O_2 = H_2O	64	1600 K, dec. with incr. T H_2 added, TMS
H_2 + ½ O_2 = H_2O	7	H_2O added, TMS
Near or at Equilibrium		
K_2O(c, slag) = 2K + ½ O_2	~ 1	Obs. in various slags
FeO(c, illite) = Fe + ½ O_2	0.36	1800 K
SiO_2(g) + H_2 = SiO + H_2O	5.9	2000 K
SiO_2(g) = SiO + ½ O_2	0.2	2000 K
Na_2CO_3(c) + 2C(c) = 2Na + 3CO	~ 1	800 K

The effect of typical sulfur and halogen-containing combustion gases on alkali vapor transport, from a commercially common soda-lime-silica glass was also modeled. This system is of interest because of its proposed (General Electric) use as a fine particle trapping medium in pressurized fluidized bed combustors combined with a downstream gas turbine unit. Typical data are shown in figure 4. These results clearly indicate the release of alkali species to the gas phase at concentrations in excess of the 10^{-7} atm limit, at 1200 K, required for minimal hot corrosion and practical turbine durability lifetimes.

Another modeling activity dealt with the possible vapor transport of Na and K as P-containing species, present as coal impurities. Based on our earlier experimental flame data on Li, Na and P-containing flames, Gibbs energies and related thermodynamic functions were estimated for the MPO_x (M = Li, Na, K; x = 2 and 3) vapor species. The thermodynamic computer models predict that, when incorporated into combustion atmospheres, these species will be a significant form of alkali. This thermodynamic data base and chemical model was also made available to the Aerodyne Research Laboratories for their MHD modeling activities. Using these results they were able to resolve severe discrepancies among workers concerning the role of P-impurities (from coal) on MHD plasma-conductivity, and hence thermal efficiency. The issue involved, on the one hand, observation of a large reduction in electron concentration (and hence MHD efficiency) for plasmas containing similar quantities of potassium and phosphorous versus a negligible effect when the potassium concentration greatly exceeded that of phosphorous. The latter condition more closely approximates normal MHD plant design conditions and the model indicates that production of KPO_2 and KPO_3 species effectively removes the electron scavengers PO_2 and PO_3 from the plasma. This effect is predicted to improve enthalpy extraction by about 60 percent and is therefore of great significance to the economic viability of MHD.

Characterization Methodology for High Temperature Gaseous Service Environments. Subtask 2 of Task 12112

J. W. Hastie, P. K. Schenck, L. H. Grabner

Objectives of this subtask are to develop and optimize measurement techniques for characterizing high temperature gaseous environments, including flames, and to apply the methodology to assessing and predicting the performance of materials in those environments. The application of classical absorption spectroscopic methods to temperature and OH concentration measurement in seeded flames was refined to minimize the troublesome effects of flame-air boundary layer formation. During fiscal year 1981 several new combustion diagnostic techniques have been developed for further application to mechanistic studies of combustion modification, including flame and smoke retardance. These techniques rely on laser excitation of electronic states in atoms and molecules. We have also utilized the enhanced thermal ionization of laser excited atoms (the optogalvanic effect or laser enhanced ionization) to modify the neutral/ion ratio from which species flow and diffusion parameters can be determined.

In collaboration with the Center for Analytical Chemistry, modeling and experimental studies have continued on the collection mechanism of ions and electrons from laser enhanced ionization (LEI). Improvements in probe design have led

to unit collection efficiency for ions formed by LEI. New techniques have also been developed for measurement of ionization rates, ion mobilities, and neutral species flow velocities in flames and other high temperature environments. The flow-velocity technique utilizes LEI to locally alter the neutral species population. Since the ternary recombination process is slow, the decrease in neutral population, due to thermal ionization of the laser excited atoms, persists and diffuses outward as it follows the flow of the hot flame gases. From the time evolution of the altered population one can determine the flow velocity. This is accomplished through the use of two laser beams resonant with an absorption of a seed-species, usually sodium. The first laser beam creates the neutral depletion or "hole" while the second laser monitors the "hole" in absorption. The flow velocity can then be obtained from time of flight or phase techniques, coupled with the known spatial separation of the laser beams. Spatial resolution of 1 mm and velocity accuracy better than 3 percent are characteristic for laminar flow flames.

The temporal and spatial evolution of the atom (or neutral) depleted "hole," created by LEI can also be monitored. This has been done by rastering a weak laser beam in a region around the primary laser beam used to create the neutral atom-depletion (typically 30 to 70 percent). For a pulsed ionizing beam and continuous probe beam, the temporal evolution of the neutral atom-depletion is monitored in absorption as a function of time for each spatial element of the raster scan. In this manner, time resolved spatial maps of the "hole" were obtained at 5 μs intervals to create a "movie" of the "hole" as it diffuses outward and is transported by the bulk gas stream. Figure 5 shows selected frames of a typical "movie." Note that the movie frames are 10 μs apart in time and represent a 1.8 mm wide by 2.2 mm high portion of the flame. The laser beam (0.1 to 0.2 mm diam.) which creates the neutral atom density hole appears at the bottom center of the first three frames. Note that the laser fires at the 5 μs frame and is terminated at 25 μs. With the laser off, the dominant hole-decay mechanism is diffusion. Later frames show the "hole" diffusing out (through back diffusion of neutral sodium) and being transported up the flame at the bulk gas flow velocity (typically 14 to 16 m/s). The gradual dissipation of the "hole" results from the slow ternary recombination of ionic sodium and electrons. The flame velocity, atomic diffusion coefficient, and ion electron recombination rates may be determined from an analysis of the spatial and temporal history of the "hole." We believe that this is the first "movie" representation of a laser induced perturbation in a flame.

Another collaborative effort with the Center for Analytical Chemistry has led to a unique method for detection of trace K, Rb, and Cs concentration-levels using LEI in the near infrared. Sensitivities of better than 1 ppb (in solution) appear possible. Using this approach, coupled with the "movie" technique mentioned above, it may be possible to study the evolution of K and K^+ in coal conversion and combustion environments.

Thermophysical Properties of Solid and Liquid Tungsten
Subtask 3 of Task 12112

D. W. Bonnell

This subtask represents a joint effort between NBS, Rice University, and the General Electric Company Advanced Applications Laboratory to measure tungsten enthalpies by levitation calorimetry. Although the experiment is conducted

physically at the GE installation, NBS has been asked to participate in the design and conduction of the experiments. Tungsten is an important commercial material because of its refractory nature in non-oxidizing atmospheres at very high temperatures. The melting point has been estimated to be 3680 K. Because of the difficulty of handling tungsten at such high temperatures, most of the thermodynamic and physical properties, in the region of the melting point, are estimates. An attractive method for determining enthalpies of refractory, electrically conducting materials utilizes high frequency sample levitation and heating. For a dense material like tungsten this could present problems which may be more readily solved by conducting the experiments in space. NASA's program for Materials Processing in Space includes research to test process concepts on the ground that may be carried out in space. Such ground experiments conceivably could turn out to be sufficient.

The combined NBS-Rice-GE effort has reached the end of its second phase. This phase was intended to complete the physical connection of the Rice calorimetric system to the GE levitation facility, and establish the measurement limits of the system for the acquisition of solid and liquid enthalpy increment data for tungsten. These limits have been established, indicating that data are obtainable on solid tungsten up to the melting point with a precision comparable to prior high temperature levitation studies on lower melting metals. It appears, however, that while liquid data are obtainable, the reliability of drop successes is so low that it will be necessary to completely automate the calorimeter system in order to accommodate the extremely unreliable holding characteristics of the levitation system. A number of necessary improvements in temperature measurement have been made to allow for high quality calorimetric heat content measurements. These improvements are expected to form a model which GE will use in a variety of areas, and will hopefully provide the basis for a generally available very high temperature imaging pyrometric device.

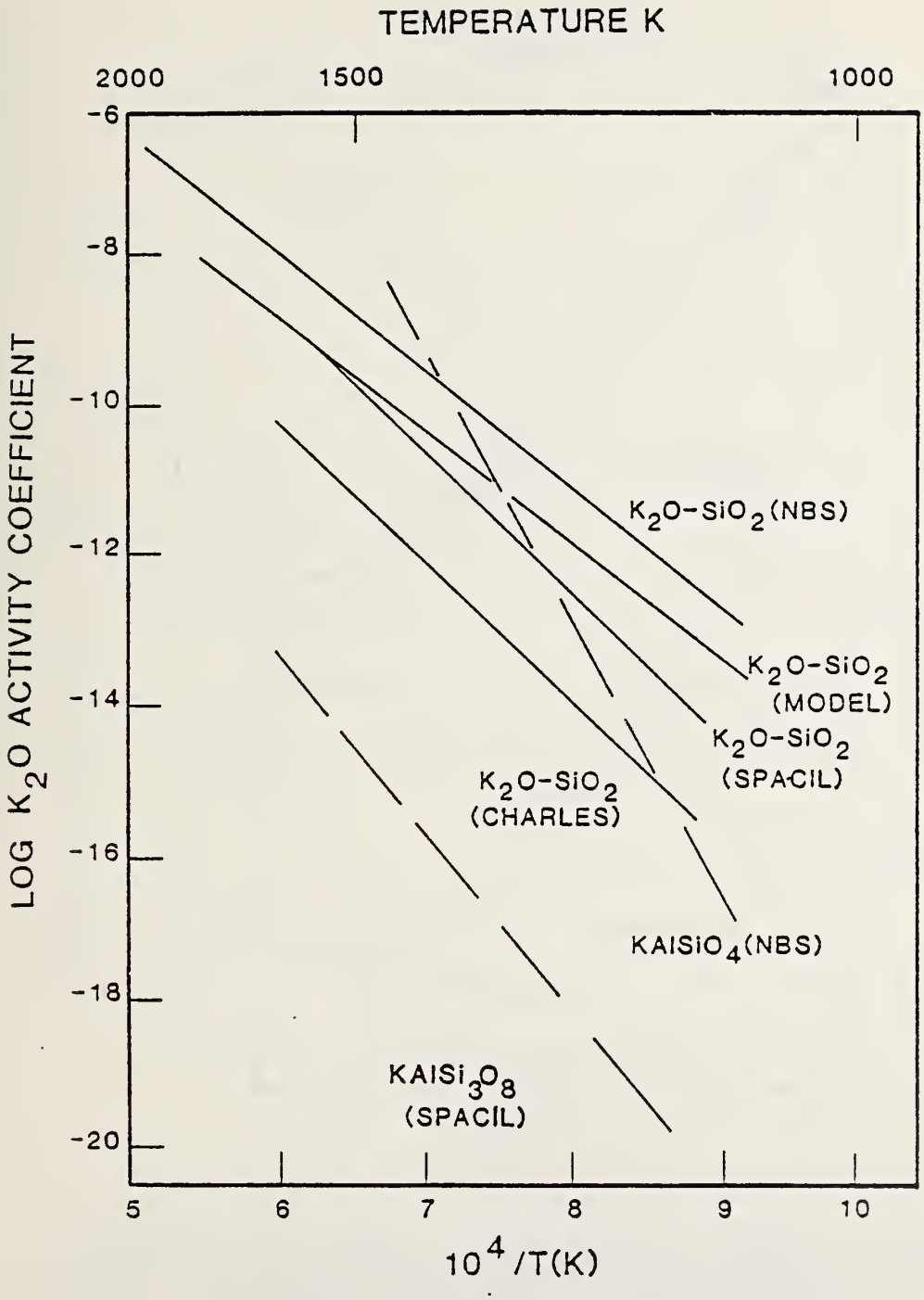


Figure 1. Comparison of K_2O activity coefficient data for the K_2O (18.8 mol %)-SiO_2 system and several K_2O-Al_2O_3-SiO_2 phases, $KAlSiO_4$ and $KAlSi_3O_8$ (SPACIL).

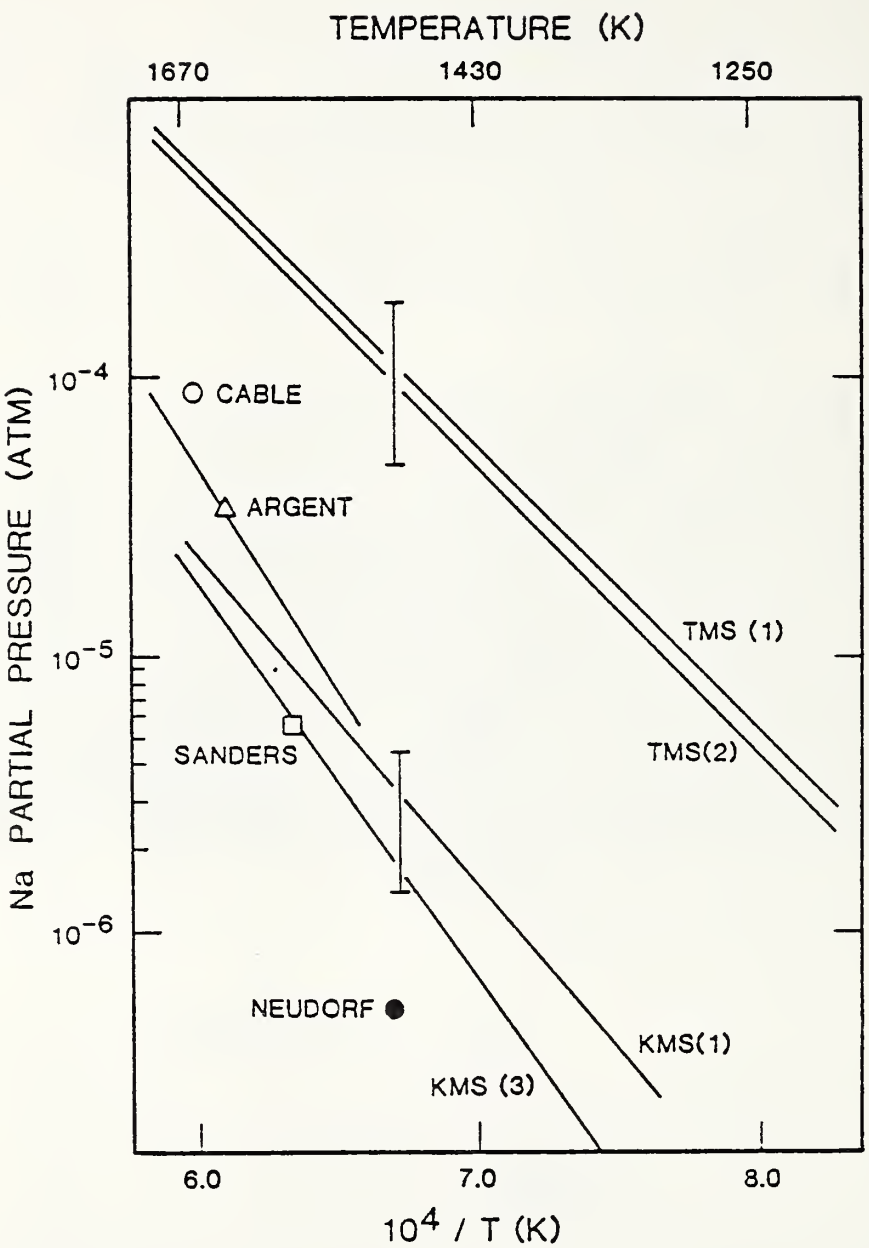


Figure 2. Comparison of glass melt Na partial pressure data obtained by various workers for compositions similar to Na_2O (17 wt. %), CaO (12%), SiO_2 (71%). KMS (1), 17.0-16.7 and KMS (2), 15.6-13.3 wt. %. The vertical bars represent the maximum conceivable errors that could arise with the KMS and TMS experiments, but as shown by the comparison of TMS (1) and TMS (2), the reproducibility is well within these limits.

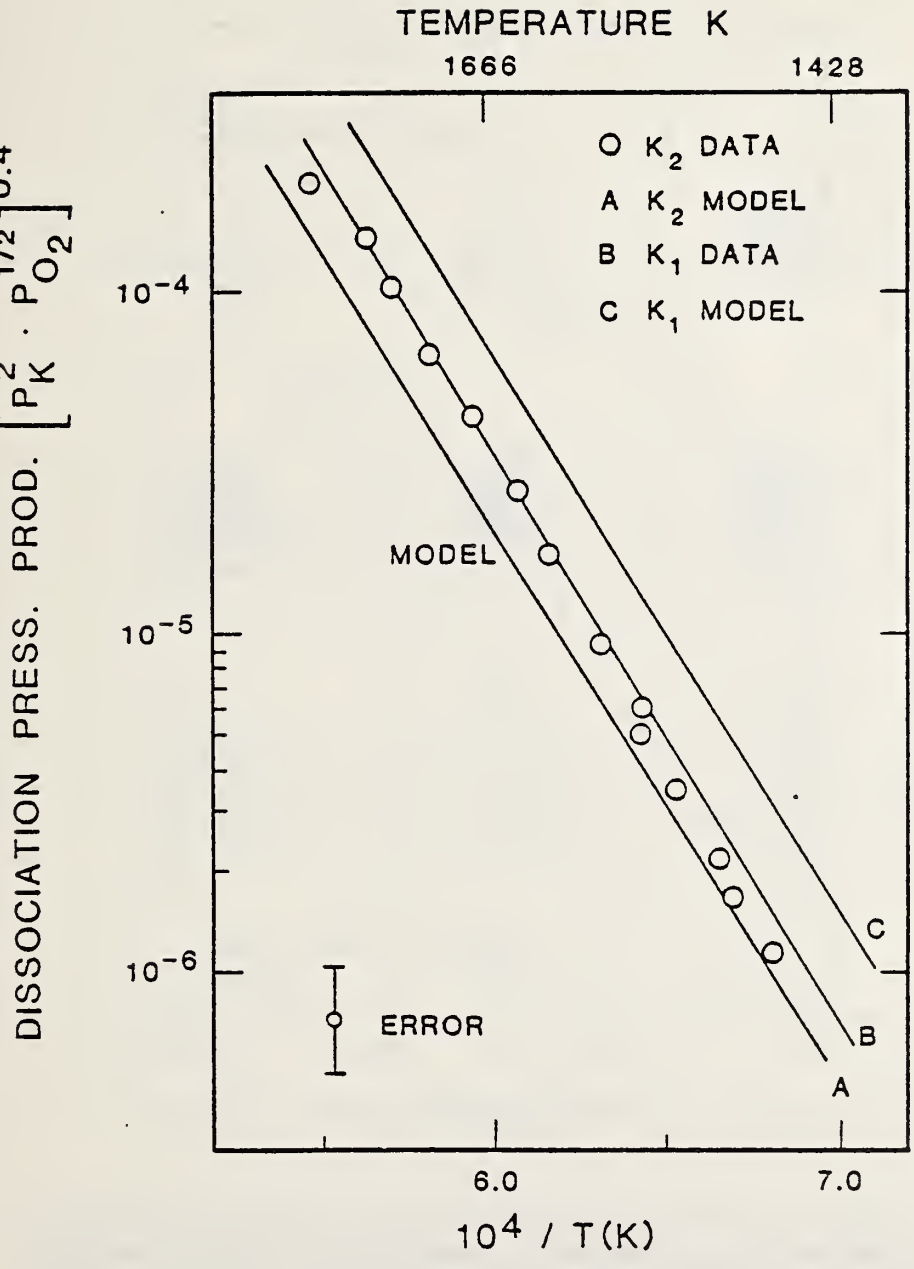


Figure 3. K_2O dissociation pressure data, where open circles represent data points for the six component K_2 slag (see table 1) and the solid curve A is the four-component model prediction. Curve B is a fit to experimental data for the real MHD slag (K_1) and curve C is the model prediction. Compositions (wt. %) are, for SiO_2, Al_2O_3, CaO, and K_2O, A = 48.8, 19.6, 25.4, and 6.2; C = 54.4, 24.7, 6.1, and 14.8, respectively.

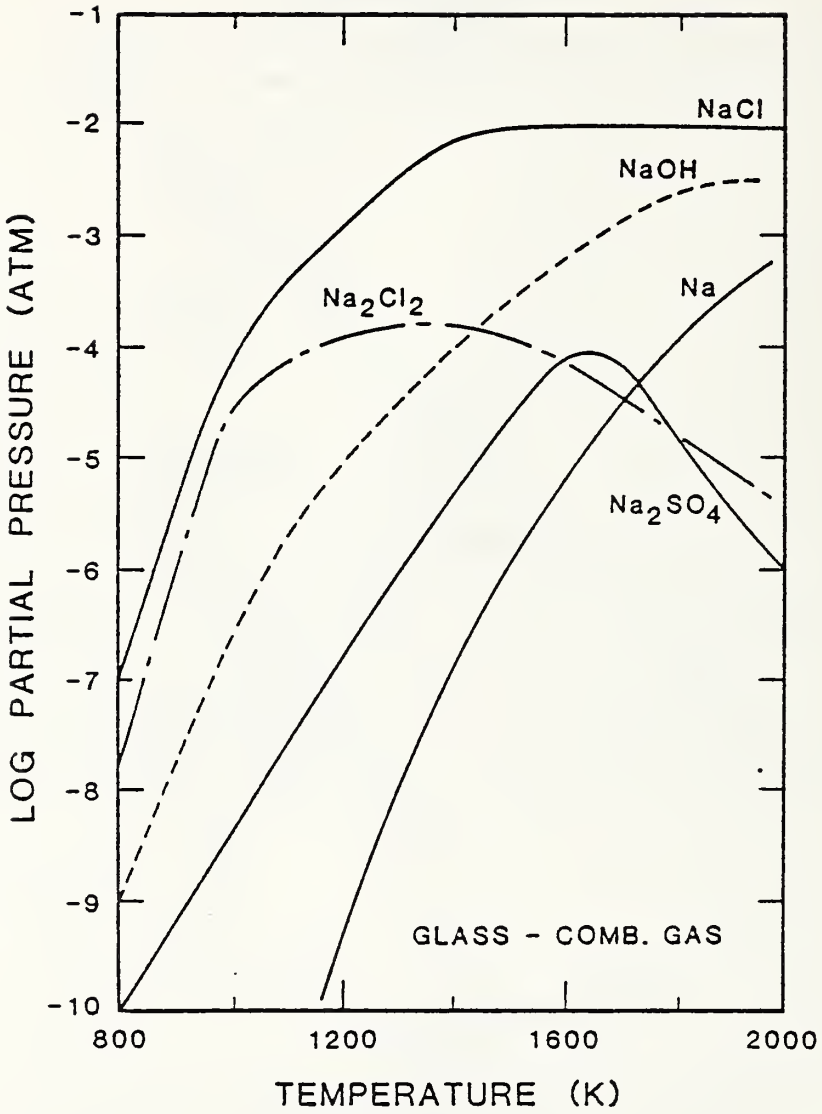


Figure 4. Computer-calculated distribution of alkali-containing species as a function of temperature for the non-ideal solution glass-combustion gas system: H_2O (4 mol %), O_2 (5), CO_2 (12), N_2 (76), SO_2 (2), HCl (1), at 1 atm. See figure 2 for glass composition.

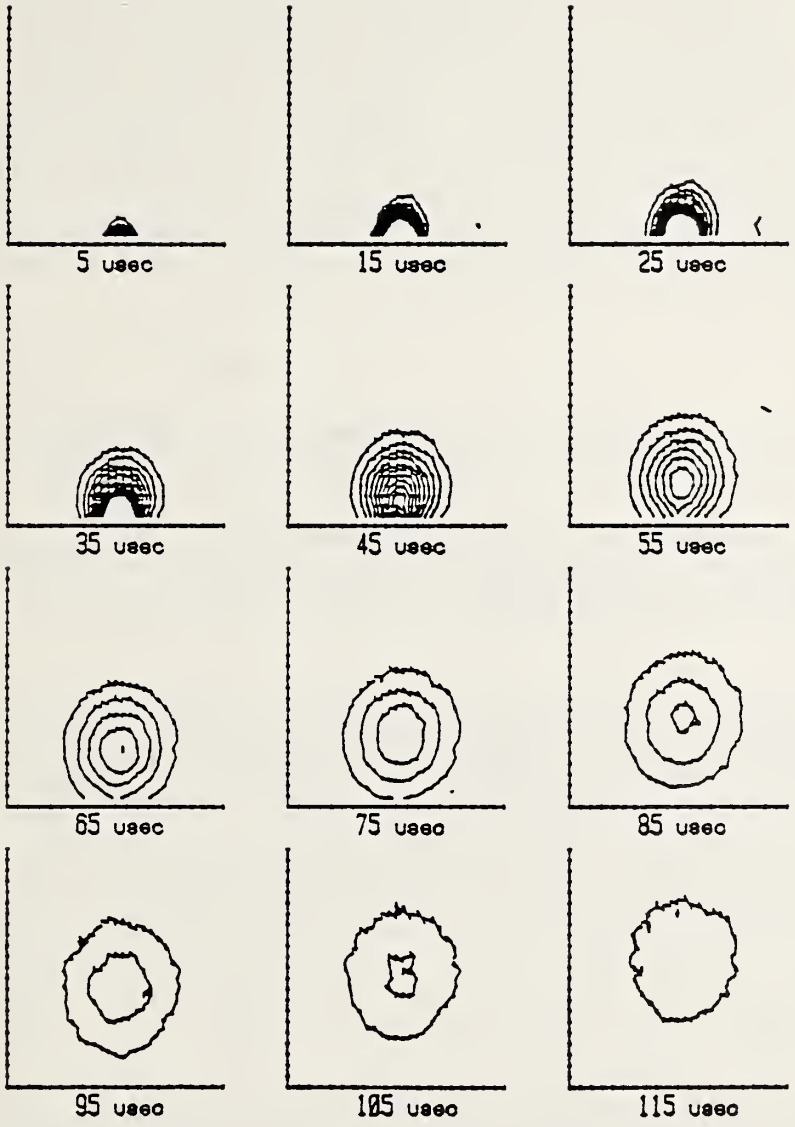


Figure 5. Computer contour plot (1 % increments in signal intensity) of LEI produced "hole" dissipation in a Na-seeded air-acetylene flame. Tick marks represent 0.1 mm spacing.

RECYCLED OIL PROGRAM--Division 561 Activities

The Tribochemistry Group of the Chemical Stability and Corrosion Division has the special assignment of providing a technical base of data and measurement methodology to support the Bureau's Recycled Oil Program (ROP). This Program is mandated by Congress under the Energy Policy and Conservation Act to provide test procedures which can be used to establish the substantial equivalency of virgin and recycled oil products. At the same time, the Group provides, within the Center for Materials Science, major scientific and technical competences in tribology and chemical stability of complex organic mixtures at metal surfaces, chemical reaction kinetics, friction and wear of materials, and detailed chemical characterization of complex organic molecules such as lubricants and fuels.

Tribochemistry
Subtask of Recycled Oil Program

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Current technical effort is directed mainly toward development of measurement methods and standards for re-refined lubricating oils used as automotive lubricants, and to develop basic scientific competences in tribology and energy-related areas.

The most important requirement for assuring the quality of re-refined motor oil is development of a set of test procedures capable of monitoring the quality, consistency, and additive response of the basestock between periodic engine sequence test qualifications. These test procedures are crucial in order to accommodate re-refined oils within the existing API-SAE-ASTM classification system. (Note: API = American Petroleum Institute; SAE = Society of Automotive Engineers; ASTM = American Society for Testing and Materials.) Development and evaluation of these tests by NBS are particularly difficult because no such set of test procedures exists for virgin lubricating oils. Historically, virgin oil producers were instead required to control the crude source and refining technology. This option is not applicable to oil recyclers.

There has been sufficient engine testing on re-refined oils to establish that: (1) a high quality re-refined lubricating oil which has been formulated with a high quality additive package can be comparable to a virgin oil similarly formulated, and (2) that both will provide adequate performance in most types of automotive service. The problem which exists at the present time is the lack of technical information and data to determine which tests are necessary and how often they should be applied in order to assure that the re-refined oil basestock is consistent between the engine tests.

At NBS the program is underway to evaluate the chemical and physical test procedures used on lubricating oil basestocks, as well as to perform research and development on bench-scale performance tests to establish basestock additive response.

In the past year significant progress has been made in achieving the goals of the recycled oil program. Laboratory evaluations of physical and chemical property test procedures are mostly complete. The ASTM/NBS basestock consistency

study, the most extensive study of its kind, has been completed, and efforts to analyze the massive volume of data are beginning. A major accomplishment is the development of a novel, fast, large-scale separation technique using preparative high pressure liquid chromatography to separate complex organic mixtures into saturates, aromatics, and polar molecules with excellent material balance. We have also developed a laboratory wear test procedure, using a four-ball configuration, which correlates with full-scale engine dynamometer sequence test. A high pressure chemiluminescence thin-film oxidation apparatus has been designed and is being built. This technique will enable us to elucidate oxidation mechanisms of organic molecules reacting with various metal surfaces. A bench oxidation simulation test of the lubricant degradation in engines has been developed using a combination of fuel components, metal catalysts, and nitrogen dioxide. Initial results suggest correlation with engine test for multigraded motor oils.

There are six project areas in the tribochemistry group: physical properties, chemical properties, hydrocarbon separation and characterization, oxidation stability, friction and wear, and NBS/ASTM Basestock consistency study. These projects are described below.

Physical Properties. Nine test methods have been evaluated for the Recycled Oil Program. These test methods were: color, pour point, kinematic viscosity at 40 °C, kinematic viscosity at 100 °C, viscosity index, API gravity, density at 20 °C, flash point, and simulated boiling range distribution by gas chromatography. Ten re-refined and seven virgin base oils were chosen to aid in establishing the test's applicability to re-refined base oils. Test method evaluations along with any necessary modifications were submitted in reports to the Recycled Oil Program Office. The data base accumulated through this effort has provided an invaluable starting point for computer correlation programs. These programs can help characterize the quality of the base oils and also correlate simpler and less expensive physical property tests to more sophisticated structural group analysis methods. In addition, the data base could allow these oils to serve as reference materials for testing by various organizations and groups.

The physical property laboratory has been utilized by the Office of Standard Reference Materials (OSRM), Center for Analytical Chemistry (CAC) of NML, Center for Mechanical Engineering and Process Technology (CMEPT) of NEL, and the Polymer Science and Standards Division of CMS.

Chemical Properties. The chemical properties of lubricating oil base stocks can be used to characterize a lubricating oil in terms of impurities and compositional characteristics critical for performance of the lubricant. Evaluation of various chemical test methods for the measurement of significant properties is under way. Among these are carbon residue, ash, and infrared absorption spectroscopy, nitrogen, and sulfur content.

Carbon residue refers to the carbonaceous material remaining after pyrolyses or destructive distillation of a 4g sample of oil in a coking furnace maintained at 550 °C (ASTM D524). A set of ten re-refined stocks and nine virgin stocks representing current production technology were used in the test evaluation. Carbon residue values for the lubricating base oil set range for re-refined base oils from 0.12 to 0.27 percent with a mean of 0.20 percent. The virgin

stocks ranged from 0.050 to 0.16 percent with a mean of 0.083 percent. Re-refined stocks thus appear to have significantly higher values of carbon residue than the virgin stocks. Work directed at understanding the basis for the significant difference has involved the determination of carbon residues of hydrocarbon type fractions, and analysis of the carbon residues for both virgin and re-refined stocks.

A tentative correlation has been observed between the polycyclic aromatic content and carbon residue value. Polycyclic aromatic content of a base oil may be determined using the Institute of Petroleum method IP 346/80 which employs a series of dimethylsulfoxide extractions. Carbon residues have been determined on major hydrocarbon type fractions of several base oils separated using high pressure liquid or column chromatographic techniques. The polar/aromatic fractions appear to be the major contributors to the carbon residue as compared with the paraffinic fraction.

Infrared absorption spectroscopy is an important method for the identification of complex hydrocarbon molecules. Software is operational for the infrared data station allowing automated spectral searches of the present commercial library of 1800 compounds. This library is being expanded to include petroleum additives as well as complex hydrocarbons commonly found in petroleum oils. This system will enhance our ability to characterize important components which affect the performance of the finished lubricant.

Nitrogen compounds can critically affect the stability of petroleum oils. Methods for the determination of total nitrogen content and "basic" nitrogen (i.e., those which neutralize strong acid) content of lubricant basestocks were investigated and modified to permit detection of as little as 1 ppm nitrogen. Total nitrogen was determined by a modified Kjeldahl procedure including preconcentration of nitrogen compounds in an acid extract. Basic nitrogen was determined by perchloric acid titration. Both methods were applied to samples of virgin and re-refined lubricant basestocks containing from 1 to 120 ppm nitrogen.

Sulfur is present in varying forms and concentrations in all crude oils. Naturally occurring sulfur may have beneficial or adverse effects on lubrication properties. Additives containing sulfur act as oxidation inhibitors. Total sulfur content is a significant parameter used to help predict performance, processing and hydrocarbon type of lubricating base oils. In addition to the performance aspects, corrosion and emissions are major concerns of sulfur-containing base oils. Six methods have been surveyed, and a high temperature combustion-titration method was evaluated. Results indicate good agreement with other methods and the method can be applied to re-refined base oils satisfactorily.

Hydrocarbon Separation/Characterization. Lubricating oil basestocks are complex mixtures of several types of hydrocarbons such as saturates, aromatics, and polars. A detailed molecular composition is critical to their performance, especially the polar type hydrocarbons. These minor constituents comprise the most active molecular species in a lubricating base oil. The structural characteristics of these active species will provide information with regard to their lubricating effects on performance of the basestocks.

This portion of the program is concerned with the methodology for the separation of base hydrocarbon materials into aromatic, saturate, and polar fractions. Prior preparative chromatographic methods are capable only of milligram quantity separation of hydrocarbon mixture. This is sufficient for chemical studies, but insufficient for most performance tests. A novel, multigram preparative HPLC method has been developed using clay-activated alumina-silica gel dual columns. Analysis of the fractions indicates clean separation of molecular types. The separation procedure consists of two steps. The basestock is first eluted on a clay column into saturate/aromatic and polar fractions. The saturate/aromatic fraction is further separated on a dual packed silical gel/ alumina column into saturate and aromatic fractions. The mass balance of this preparative HPLC method is excellent and the fractions produced are pure and ready to be used for further evaluation.

Spectroscopic methods such as IR, UV, high field NMR, and mass spectrometry, as well as gel permeation chromatography (GPC) have been applied to elucidate structural characteristics. In cooperation with the Chemical and Biodegradation Processes group, high field NMR results suggested the presence of polyisobutylene (probably from the viscosity index improver additive) in some of the polar fractions from re-refined base oils.

Oxidation Stability. In the area of performance tests for automobile crankcase oils, the industry-accepted tests include the current engine sequence tests (IID, IIID, VD, L-38), laboratory truck engine tests (1H2, 1G2, EMD, T02), full-scale truck engine tests (Mach T-6), fleet tests (Aunt Minnie type, taxi/police fleet heavy duty type, commuter type, tire-track, and EPA cycle type). The expenses involved in running these tests are enormous. There are no commonly accepted laboratory bench tests for indicating in-service performance.

The performance requirements of an automobile lubricant are rust and corrosion protection, detergency, solvancy (to solubilize oxidized products), high temperature stability (to keep piston rings from sticking), viscosity-temperature characteristics (to maintain hydrodynamic lubrication), anti-wear properties, and low frictional resistance. The oxidation stability of oils is common to most of these requirements.

The program plan of the performance testing areas will make use of ASTM Reference Oils as a tool to screen promising procedures. The reference oils are currently being used to monitor all the certified engine test stands in the various testing laboratories all over the United States and in some foreign countries. These oils can be classified into good, bad, and borderline performance oils. By using these reference oils, test procedures can be screened for correlation with in-service performance. Test procedures studied in the past year include oil thickening test, and the rotary bomb oxidation test. In addition, competence in thermal analysis, chemiluminescence, high pressure thin film oxidation tests have been developed.

Oil thickening in engines is primarily caused by oxidation of oil at high temperature engine operation, and is catalyzed by the presence of wear metal compounds, unburned or partially burned fuel components, and nitrogen dioxide in the blow-by. A bench oil thickening test is presently being developed by simulation of these chemical environments. The goals of the work are to achieve a correlation between bench test and engine test results, and to understand the mechanism of oil thickening.

At present, six reference oils have been tested under various conditions: (1) different fuel catalysts, (2) different metal catalysts, and (3) with or without the presence of nitrogen dioxide. So far, best results were found when a synthetic fuel catalyst was used with a metal catalyst system containing lead, iron, copper, manganese, and tin at the presence of nitric dioxide. The test conditions were as follows:

100 g oil
175 °C
80 cc/min air plus 2000 ppm NO_2
Synthetic fuel catalyst (TAN = 2), 10 percent
Metal catalyst (napthenates)

Cu	0.069%
Fe	0.41%
Pb	8.00%
Mn	0.35%
Sn	0.36%

The composition of the metal catalyst is determined based on the information on used oil analyses. The steps for making the synthetic catalyst are developed as shown in figure 1. They apply the concepts used by Verley [1] and Forbes [2] in their work for VD bench test development. As shown, a gasoline fraction (150 °C) is oxidized and the product is standardized by neutralization with sodium bicarbonate solution to a constant acidity. Neutralization removes excess active acid oxidation precursors which may react with base detergent additive in the oil and cause unnecessary load to the oils. The final synthetic catalyst should have a total acid number of 2.

Test results of six reference oils under the above conditions are given in table 1, and are compared with IIID test results. As shown, partial correlation has been obtained between the two tests. Among the four multi-grade oils, the bench test gives good correlation with the engine test; but not among the two single grade oils. One possible explanation for lack of correlation in single grade oils may be due to different antioxidant used in these two oils, and higher viscosity base oils. Future research will focus on further development of a selective catalyst which attacks the antioxidant used in the single-grade oils.

The Rotary Bomb Oxidation Test (ASTM D2272) is being evaluated for the determination of the oxidation stability of virgin base oils and re-refined base oils. The test results of three virgin base oils and three re-refined base oils under standard test conditions (5 cc water, copper catalyst, 150 °C) are summarized in table 1. As shown, the oxidation stabilities of the re-refined base oils are as good as those of virgin base oils. The induction times of re-refined base oils range from 44 min to 61 min and those of virgin base oils fall between 45 min to 59 min.

As indicated in table 2, the results of all tests are repeatable within six percent. This improved repeatability has been achieved by modification of the oxygen feed system through installation of a precision pressure gauge to control the initial oxygen feed pressure to the bomb. With this modification, repeatability has been improved from ten percent to six percent.

Although the tests at standard conditions do indicate, to a certain degree, the oxidation stability of base oils, these conditions have been developed primarily for steam turbine oils. The standard test condition may not reflect the real service conditions of the base oils. In automotive engines, the base oil encounters less water, iron catalyst is present in addition to copper, and nitrogen dioxide is present from blow-by gases. Thus, modifications of the standard test conditions for base oils are in progress. Preliminary data indicate that water content and type of catalyst affect significantly the induction time of a base oil. It has been found that the induction time of the oil increases with the decrease in water content and with the use of iron catalyst. Further experiments are in progress.

Oxidation Kinetics. Oxidation kinetics of lubricating oils can be studied by oxygen-uptake experiments. Most of this type of work has been done by using a circulatory system in which oxygen is pumped through the oil in a closed system and the oxygen absorbed by oil is determined by volume difference of O_2 at constant pressure. Typical studies using circulatory type apparatus were reported by Dornte [3] and Chao [4].

A static oxygen uptake system is being designed. In this system, a thin film of oil is placed on a metal disk serving as catalyst, and the oxygen absorbed by the oil is determined by the pressure change of the system through a pressure transducer. Thin film technique can eliminate effects of diffusion limitations, and ensure the measurement of true oxidation rate of oils. A simple mathematical model has been developed to estimate the maximum film thickness. It was found that for most of the oils the desired film thickness is in the order of a hundredth of a centimeter.

The system is designed to operate at high pressure and high temperature. High pressure suppresses the evaporation of oil at the high temperatures of experiment, and thus reduces the vapor phase oxidation. The maximum pressure of the system is designed at 1000 psi, and the maximum temperature at 300 °C. Literature search has indicated that very little work has been reported at these conditions.

The system is also designed to couple with a fiber optic probe to study the chemiluminescence of oil during oxidation. Combining the oxygen uptake and chemiluminescence measurements of an oil, oxidation rate constants and activation energy of the basic oxidation steps can be obtained. Chemiluminescence provides an extremely sensitive means of determining low and high temperature degradation and oxidation of fuels and lubricants. The stability and additive response can be evaluated in a short time period and a small quantity of sample. The chemiluminescence apparatus has been designed and initial experiments are underway. A literature review of fuel and lubricant applications of the chemiluminescence technique has been completed.

A Differential Scanning Calorimeter (DSC) and a Thermogravimetric Analyzer (TGA) were acquired to support our effort in analysis and characterization of oils. Thermodynamic and kinetic properties relating to oxidative stability, gum formation, molecular size distribution, volatility, thermal stability, and cold handling can be assessed. Tests to date indicate that the test procedures which we are developing will become integral parts of our analysis and characterization schemes for oil fractions, oil basestocks, and formulated oils.

Friction and Wear. Emphasis in this area has been divided into two parts. The first part deals with investigating the chemical aspects of friction and wear. The second part deals with the evaluation of various four-ball test methods for their ability to measure the wear performance of lubricating motor oils.

A study was conducted to determine whether impurities normally found in base oils had any effect on wear performance of a base oil. A re-refined base oil was separated into three fractions using open column chromatography. A pure fraction (paraffins), a pentane eluted fraction (mostly paraffins and some aromatics), and an acetone eluted fraction (polars). Various amounts of the acetone eluted fraction (polars) were reblended into the pure fraction. Wear tests were run on these blends and the following observations were made. (1) For a pure base oil small amounts of impurities were beneficial, i.e., wear was reduced. (2) For a base oil with 0.5 percent antiwear additive small amounts of impurities reduced the effectiveness of the antiwear additive, i.e., wear was increased above that of the pure oil plus the additive. (3) Over a period of time, larger amounts of polars completely eliminated the beneficial effect of the antiwear additive, i.e., the antiwear additive failed to decrease wear as it had in the pure base oil.

Four-ball wear test methods were evaluated using a set of six ASTM IIID engine sequence test reference oils. These reference oils have a significant data base and have shown a correlation to actual field performance. Wear data obtained from engine sequence tests shown in table 3 indicate that the oils can be roughly classified as high or low wear oils.

A preliminary parametric study at a variety of speed/load combinations failed to show correlation except at 200 rpm and 200 lb load. Wear test results at these conditions (table 3) show a slight correlation with IIID results. Since high load wear performance seemed to be important, two procedures for evaluating the high load performance of lubricants were investigated.

The first procedure, a load capacity test, evaluates the ability of a lubricant to carry a load. This is accomplished by running a series of wear tests at different loads. When the load of the test exceeds the capacity of the lubricant the lubricant film breaks down and wear and friction increase drastically. The highest load that protects against this accelerated wear condition defines the load capacity of the lubricant. The higher the load capacity, the better the lubricant. Results from the load capacity tests shown a correlation with engine sequence test results.

The second procedure that was evaluated was a step loading seizure test. This test also provides a relative rating of the ability of a lubricant to carry a load but this is accomplished running a single test instead of a series of tests. Results obtained from this test also correlated with IIID engine test results (table 3).

A new small sample wear test is currently under development. This test uses only 6 µl of lubricant for each test. This test will allow more extensive testing on the chemical aspects of friction and wear. This is best accomplished with a micro sample test because only small amounts of the active components can be isolated for study. Initial results from a micro sample step loading seizure test have already shown a correlation with IIID results.

We are currently participating in round robin for ASTM Tech L XI-8 to evaluate a test procedure that measures the coefficient of friction for fuel efficient motor oils.

ASTM/NBS Basestock Consistency Study. In conjunction with ASTM, we have sponsored a study to collect information and data to determine which tests are necessary and how often they should be applied in order to assure that the re-refined basestock is consistent between the engine tests.

The user industries are concerned about the potential lack of consistency of re-refined oil products, and about the potential effects of re-refineries. These potential problems are of particular concern when warranty questions are involved.

In this one-year study, four virgin oil producers and six re-refined oil producers are submitting monthly samples for analysis by a group of 12 organizations, including NBS (table 4). These laboratories will analyze the coded samples using over 40 different chemical, physical, and performance tests. The program was started in March 1980 and has been successfully concluded this year.

A partial impression of the results of the study may be gleaned from some NBS data shown in tables 5 and 6. In each table, oil producers are designated by a letter from A through K. Producers A, B, C, D, and I are virgin oil refiners. The months indicate month of producton, except in the case of control sample I, which was the internal standard.

Moisture content of most (table 5) was generally between 50 and 150 ppm. Only re-refined oils F and G exhibited many exceptional month-to-month variations in moisture content.

Refractive index (table 6), a bulk oil property, shows small month-to-month variations in all oils, with no clear consistency difference between virgin and re-refined oil. The magnitude of refractive index of re-refined oils is slightly larger than that of virgin refined oils.

References

[1] Vertley, G. M., U.S. Patent 3,044,860 assigned to Sinclair Research, Inc., 1962.
[2] Forbes, E. S., and Wood, J. M., I&EC Product R&D 1, 48 (1969).
[3] Dornte, R. W., I&EC 28, 26 (1936).
[4] Chao, T. S., Kjonaaf, M., Vitchus, B. C., SAE Paper No. 700890 (1970).

Table 1

Multi-grade Reference Oils

Oil	Time to reach 400% Viscosity increase, h	Sequence III D engine test results
76A-1	39	PASS
75B-1	37	PASS
79A	35	PASS (borderline)
78B-1	31	FAIL
	Single grade Reference Oils	
77C	56	FAIL
72A-1	60	FAIL

Table 2

Summary of RBOT Data
Induction Time in Minutes

50 g oil
5 cc water in oil
150 °C
90 psig O_2, Copper Coil

Re-refined Oil			Virgin Oil		
RB0023		43	VB5169		45
		45			47
		45			42
	Avg.	44		Avg.	45
	St. Dev.	1.2		St. Dev.	2.5
	% Dev.	2.7		% Dev.	5.6
RB0033		57	VB5078		59
		60			56
		56			63
	Avg.	58		Avg.	59
	St. Dev.	2.1		St. Dev.	3.5
	% Dev.	3.6		% Dev.	5.9
RB0062		63	VB5090		49
		59			39
		61			42
	Avg.	61		Avg.	40
	St. Dev.	2.0		St. Dev.	1.5
	% Dev.	3.2		% Dev.	3.8

Table 3

Four-ball Wear Data on ASTM Sequence IIID Engine Test Reference Oils

Test Description	Reference Oils 76A	75A	79A	77B	77C	72A-1
Sequence IIID Engine Wear Test						
Cam + lifter wear ($cm \times 10^{-4}$)	48	46	48	287	277	256
Wear classification	low	low	low	high	high	high
Four-ball Wear Test						
Slow sliding test[1] (wear scar, mm)	0.51	0.51	0.50	0.55	0.60 (seizure)	0.60 (seizure)
Load capacity test[2] (load capacity, kg)	135	135	135	120	105	90
Step loading seizure test[3] (seizure load, kg)	200	209	218	168	132	132

[1]condition: 200 rpm, 200 lb, 75 °C, Falex #6 4-ball wear tester.
[2]condition: 200 rpm, 75°C, Roxann 4-ball wear tester.
[3]condition: 200 rpm, 9 kg (20 lb) increments, 5 min/load, Falex #6 4-ball wear tester.

Table 4

Organizations Cooperating in the ASTM/NBS Basestock Consistency Study and the Tests

Organizations

Bartlesville Energy Technology Center
Chevron, USA
Gulf R&D
Lubrizol
Mobil Oil Corporation
National Bureau of Standards
National Research Council of Canada
Suntech, Inc.
Texaco
U.S. Army MERADCOM

Tests

Physical Property Tests

Demulsibility
Filterability
Gravity
Color
Cold Cranking Simulator 0 to -40 °C
Mini-rotary Viscosity 10 to -40 °C
Brookfield Viscosity 0, -20, -40 °C
Viscosity at 40 and 100 °C
Viscosity Index
Refractive Index
Pour Point
Carbon Residue
Boiling Point Distribution
Foam

Chemical Property Tests

Tota Acid Number
Saponification Number
Nitrogen, Sulfur
Hydrocarbon Type by Mass Spect.*
Hydrocarbon Type by Liquid Chromatography
Emission Spectrograph
Halogens
Differential Infrared
Sunlight Stability
Additive Compatibility
Glycol Content

Bench Tests

Additive response to oxidation*
Additive response to wear*
Rusting
LUBTOT
Seq III C Simulator
Foro Anti-oxidant Response
Differential Scanning Calorimetry
RBOT (Basestock + Additive)
Turbine Oil Oxidation*

*On selected samples

Table 5
Refractive Index of Lubricating Base Oils

	virgin base oil			Control Sample	re-refined base oils						
MONTH	A	B	C	D	I	E	F	G	H	J	K
MARCH	1.4749	--	1.4788	1.4793	1.4837	1.4809	1.4838	1.4839	1.4856	1.4864	1.4826
APRIL	53	1.4814	796	90	35	03	37	49	53	69	
MAY	49	20	797	87	36	04	32	45	52	61	
JUNE	46	18	804	86	36	06	40	78	39	46	
JULY	55	23	819	96	36	06	39	43	38	59	
AUGUST	70	25	818	88	36	06	40	50	46	48	
SEPTEMBER	73	31	832	89	36	17	38	41	29	47	
OCTOBER	75	26	830	85	31	17	30	44	51	42	
NOVEMBER	67	30	815	82	36	13	32	24	40	50	
DECEMBER	74	26	810	84	36	29	36	30	36	52	
JANUARY	80	24	819	81	35	--	28	34	41	47	
FEBRUARY	81	31	811	81	35	--	34	31	36	58	49
MARCH	84	55	809	82	36	--	41	31	43	42	49
MEAN	1.4766	1.4827	1.4811	1.4786	1.4836	1.4811	1.4836	1.4841	1.4843	1.4853	1.4841
STD. DEV.	14	10	13	5	1.4	8	4	14	8	9	13

Table 6
Moisture Content (µg/g) of Lubricating Base Stocks

	virgin base oil			Control Sample	re-refined base oils					
MONTH	A	B	C	D	I	E	F	G	H	J	K
MARCH	51	--	60	80	63 71	100	82	111	97	70	108
APRIL	51	139	442	44	65	82	101	412	94	103	--
MAY	57	136	75	51	87	102	77	254	83	134	--
JUNE	54	120	77	45	59	132	301 288 298	147	78	88	--
JULY	59	155	98	70	71	109	96	131	151	75	--
AUGUST	65	146	52	53	52	201	91	136	100	87	--
SEPTEMBER	72	155	58	29	54	93	102	203	NT	56	--
OCTOBER	72	148	67	59	62	76	50	116	NT	86	--
NOVEMBER	47	106	42	40	53	100	313	114	70	88	--
DECEMBER	40	145	52	26	53	117	313	87	NT	89	--
JANUARY	44	122	51	36	61	--	99	109	NT	76	--
FEBRUARY	54	149	69	49	53	--	67	103	NT	56	205
MARCH	46	107	42	34	48	--	83	215	69	81	127
MEAN	55.1	135.6	91.1	47.3	60.6	111.2	135.5	164.4	92.7	83.7	146.6
STD. DEV.	9.7	17.6	106.5	15.6	10.7	35.4	97.6	89.5	26.3	20.1	51.4

NT: Non-titratable due to gum formation on electrode

Other Activities of the Chemical Stability and Corrosion Division

Invited Talks

High Temperature Chemistry of Phosphorus-Containing Flames
Chemical Stability and Corrosion Division Seminar
National Bureau of Standards, Washington, D.C.
J. W. Hastie
July 16, 1980

Levitation Calorimetry
Electric Field Positioning Science Working Group Organizational Meeting, Baltimore, Maryland
D. W. Bonnell
September 10, 1980

NMR Spectroscopy
ASTM Symposium, Philadelphia, Pennsylvania
R. B. Johannesen
September 29, 1980

The Protection of Steel Piles by Metallic Coatings in Sea Water
Plenary Lecture, 5th Latin American Reunion on Electrochemistry and Corrosion, Concepcion, Chile
E. Escalante
September 29, 1980

Progress in Laser Enhanced Ionization
FACS Meeting, Philadelphia, Pennsylvania
J. C. Travis, G. C. Turk, P. K. Schenck
September 30, 1980

Electrochemical and Ellipsometric Studies on Iron in Highly Alkaline Solutions
Electrochemical Society, Hollywood, Florida
J. J. Ritter
October 7, 1980

Passivity and Breakdown of Passivity
Case Centennial Symposium on Electrochemistry in Industry--New Directions
Case Western Reserve University, Cleveland, Ohio
J. Kruger
October 22, 1980

High Temperature Calorimetry
Containerless Processing Workshop, King of Prussia, Pennsylvania
D. W. Bonnell
October 27, 1980

Volatilization of Mercury by Thiobacillus
Chesapeake Biological Laboratory, Solomons, Maryland
G. J. Olson
October 30, 1980

Plating on Anodized Aluminum
AES Symposium on Plating on Difficult to Plate Metals, New Orleans, Louisiana
D. S. Lashmore
October 31, 1980

Ultratrace Element-Specific Speciation of Biogenic Organometals
Carnegie Intitute of Washington Conference: Geochemistry of Organic Matter in Ore Deposits, Warrenton, Virginia
W. R. Blair
November 1980

Volatilization of Mercury by Thiobacillus ferrooxidans
Carnegie Institute of Washington Conference: Geochemistry of Organic Matter in Ore Deposits, Warrenton, Virginia
G. J. Olson
November 1980

Magnetic and Structural Properties of the $Mn_{23}Dx$, $Y_6Mn_{23}Dx$, and RFe_2Dx
12th Central Regional Meeting, American Chemical Society, Pittsburgh, Pennsylvania
V. K. Hardman
November 14, 1980

New Approaches to the Study of Localized Corrosion
Materials Science Seminar
Center for Materials Science, Johns Hopkins University, Baltimore, Maryland
J. Kruger
November 19, 1980

Basestock Requirements and Characterization
ASTM D-2, P-1 Meeting
Fort Lauderdale, Florida
S. M. Hsu
December 1980

Magnetic Properties of $Y_6(Fe_{1-x}Mn_x)_{23}$ Compounds
Materials Science Seminar
Naval Research Laboratory, Washington, D.C.
V. K. Hardman
December 5, 1980

Optogalvanic Spectroscopy
Chemical Stability and Corrosion Divison Seminar
National Bureau of Standards, Washington, D.C.
P. K. Schenck
December 8, 1980

Optogalvanic Spectroscopy
National Institutes of Health, Bethesda, Mryland
P. K. Schenck
December 10, 1980

Characterization of Macromolecules and Their Polymerization by Chromatographic Methods
147th Natonal Meeting of the American Association for Advancement of Science, Toronto, Ontario, Canada
E. J. Parks
January 4, 1981

Electrochemical Noise Measurements
Institute of Inorganic and Physical Chemistry
University of Bern, Switzerland
U. Bertocci
January 7, 1981

Impedance and Noise Measurements in Corrosion
Institute of Materials and Corrosion, Federal Engineering School, Zurich, Switzerland
U. Bertocci
January 8, 1981

Electrodeposition Research at NBS
American Electroplaters Society and Electrochemical Society Local Sections, Detroit, Michigan
D. S. Lashmore
January 12, 1981

A Review of the Work on Noise and Impedance Measurements at NBS
Institute of Physical Chemistry, University of Karlsruhe, Germany
U. Bertocci
January 13, 1981

Noise and Impedance Measurements in Corrosion
Institute of Physical Chemistry, University of Clausthal-Zellerfeld, Germany
U. Bertocci
January 21, 1981

Current Understanding of SCC in High Strength Aluminum Alloys
Golden Gate Metals and Welding Conference, San Francisco, California
E. N. Pugh
January 23, 1981

Molecular Basis for Release of Alkali and Other Inorganic Impurities from Coal Minerals, Slag, Fly Ash, and Glass
DOE Conference, Morgantown Energy Technology Center, Morgantown, West Virginia
J. W. Hastie
February 4, 1981

Plating on Aluminum
American Society for Metals, Local Section, Newark, E. Orange, New Jersey
D. S. Lashmore
February 23, 1981

A New Ellipsometric-Electrochemical Approach to the Study of Corrosion under Organic Coatings
Materials Engineering Department, Technion, Haifa, Israel
J. Kruger
February 26, 1981

New Approaches for Study of Localized Corrosion
Electrochemistry Laboratory, Tel Aviv University, Tel Aviv, Israel
J. Kruger
March 1, 1981

New Approaches to Study of Localized Corrosion
Materials Engineering Department, Technion, Haifa, Israel
J. Kruger
March 5, 1981

Neutral Atom Depletion by CW Laser Enhanced Ionization in Analytical Flames
Pittsburgh Analytical Spectroscopy Conference, Pittsburgh, Pennsylvania
J. C. Travis, G. C. Turk, P. K. Schenck, and T. C. O'Haver
March 10, 1981

Electroplating Research at NBS
Goddard Space Flight Center, Greenbelt, Maryland
D. S. Lashmore
March 18, 1981

New Approaches to Study of Localized Corrosion
Electrochemistry Laboratory, National Research Centre, Dokkai, Cairo, Egypt
J. Kruger
March 18, 1981

Corrosion Fundamentals
Physics Department and University of Maine Technical Services Program, Orono, Maine
J. Kruger
March 26, 1981

Modern Aspects and Techniques of Corrosion Study and Testing
Physics Department, University of Maine Technical Services Program, Orono, Maine
J. Kruger
March 26, 1981

Alkali Vapor Transport in Combustion Systems
High Temperature Chemistry ACS Symposium, Atlanta, Georga
J. W. Hastie
March 29, 1981

Ultratrace Speciation and Biogenesis of Methyltin Transport Species in Estuarine Waters
NATO Advance Research Institute on "Trace Metals in the Sea," Erice, Sicily
F. E. Brinckman
March 30, 1981

Measuring the Rate of Corrosion of Steel in Concrete
Corrosion 81, National Association of Corrosion Engineers, Toronto, Canada
E. Escalante
April 6, 1981

Transgranular SCC in Cu-Zn Alloys: Electrochemical Aspects
Corrosion 81, National Association of Corrosion Engineers, Toronto, Canada
E. N. Pugh
April 6, 1981

Corrosion Behavior of Some Stainless Steels in Underground Soil Environments
Corrosion 81, National Association of Corrosion Engineers, Toronto, Canada
W. F. Gerhold
April 7, 1981

An Ellipsometric-Electrochemical Study of Corrosion Processes on Iron Protected by Organic Coatings
Corrosion 81, National Association of Corrosion Engineers, Toronto, Canada
J. J. Ritter
April 7, 1981

Electrochemical Noise and Localized Corrosion
Corrosion 81, National Association of Corrosion Engineers, Toronto, Canada
U. Bertocci
April 8, 1981

Noise in Electrochemical Systems
6th International Symposium on Noise in Physical Systems, National Bureau of Standards, Washington, D.C.
U. Bertocci
April 9, 1981

Vaporization of Potassia-Containing Substances and Its Application to MHD
Chemical Stability and Corrosion Division Seminar, National Bureau of Standards, Washington, D.C.
E. R. Plante
April 16, 1981

Time Evolution of the Depleted Atom Density Following Laser Enhanced Ionization in a Flame
Chemical Stability and Corrosion Division Seminar, National Bureau of Sandards, Washington, D.C.
P. K. Schenck
April 27, 1981

Metallic Corrosion--Opportunities for Physics Research
Physics Colloquium, Brandeis University, Waltham, Massachusetts
J. Kruger
April 28, 1981

Currents in Corrosion Research
Chemical Abstracts Service, Columbus, Ohio
T. D. Coyle
May 7, 1981

Current Understanding of SCC of Austenitic Stainless Steels
Central Carolina Chapter American Society for Metals, Wilmington, North Carolina
E. N. Pugh
May 8, 1981

Application of Molecular Substituent Parameters for the Speciation of Organometals in Process Fluids by Element-Selection HPLC
DOE/NBS Workshop on Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes, National Bureau of Standards, Washington, D.C.
C. S. Weiss
May 19, 1981

Temperature Dependent Electron Impact Fragmentation in High Temperature Molecular Beams
American Society for Mass Spectrometry, Minneapolis, Minnesota
D. W. Bonnell and J. W. Hastie
May 25, 1981

Recent Progress in the Speciation of Environmental Organotins
School of Chemistry, Leicester Polytechnic, Leicester, England
F. E. Brinckman
May 29, 1981

Fractography of Stress-Corrosion Failures
NATO Advanced Research Institute on Atomistics of Fracture, Ajaccis, Corsica
E. N. Pugh
May 30, 1981

Relationships Between Biogenic or Anthropogenic Organotins in Aquatic Systems and Their Atmospheric Transport
Fifth International Symposium on Environmental Biogeochemistry, Stockholm, Sweden
F. E. Brinckman
June 2, 1981

Electrochemical Noise Measurements
CNRS Research Group on Physics of Liquids and Electrochemistry, Paris, France
U. Bertocci
July 2, 1981

Effect of Environment on Crack Extension Under Static Load
Gordon Research Conference on Physical Metallurgy, Andover, New Hampshire
E. N. Pugh
July 8, 1981

Chromatographic Speciation Methods for Studies of Arsenic Biotransformations
Office of Toxic Substances, Environmental Protection Agency, USDA Beltsville Research Center, Beltsville, Maryland
F. E. Brinckman
July 21, 1981

Structural and Magnetic Studies of $Th_6Mn_{23}D_{16}$ and $Y_6Mn_{23}D_{22}$
Gordon Conference at the Foundament and Properties of Metal Hydrides, Tilton, New Hampshire
V. K. Hardman
July 24, 1981

Occurrence of Organoarsenic Compounds in Oil Shale Processing: Molecular Diagnostics for Their Chromatographic Speciation
Tenth International Conference on Organometallic Chemistry, Toronto, Canada
C. S. Weiss
August 10, 1981

Application of Equilibrium Diagrams to Corrosion
Workshop on Setting-up and Applications of Diagrams of Chemical and Electrochemical Equilibria, CEBELCOR, Brussels, Belgium
J. Kruger
September 4, 1981

Thermodynamic Models of Vapor Transport in Silicate Systems
International Union of Pure and Applied Chemistry High Temperature Chemistry Conference, Harwell, England
J. W. Hastie, W. S. Horton, E. R. Plante, and D. W. Bonnell
September 7, 1981

Biodeterioration of Standard Reference Materials
Fifth International Biodeterioration Symposium, Aberdeen, Scotland
W. B. Iverson
September 7-11, 1981

Biological Corrosion
International Biodeterioration Working Group, University of Aston-Birmingham, England
W. P. Iverson
September 14-16, 1981

Biotransformations of Tin
International Conference on Heavy Metals in the Environment, Amsterdam, The Netherlands
W. R. Blair
September 15, 1981

Technical and Professional Committee Memberships

American Ceramic Society
S. J. Schneider, Member

Refractories Division, S. J. Schneider, Editorial Chairman

Executive Committee, S. J. Schneider, Member

American Chemical Society
Inorganic Chemistry Division--Nomenclature Committee
T. D. Coyle, Chairman

Councilor from Chemical Society of Washington, 1981-1983
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Committee on Corrosion Protection of Steel Structures
W. F. Gerhold, Member

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Joint Committee on Static Petroleum Measurement Working Group on Water and Sediment
J. J. Comeford, Member

American Society for Testing and Materials

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A05.09: Advisory, Chairman
A05.14: Sheet Tests
A05.15: Wire Tests
A05.16: Hardware Tests, Chairman

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WG.05: Metrication, Chairman
B08.03: Decorative Copper, Nickel, Chromium, and Nickel-Chromium Coatings
WG: Electrodeposited and Electroless Black Coatings for Solar Use
B08.04: Zinc and Cadmium Coatings
B08.05: Coatings of Tin, Lead, and Their Alloys
B08.06: Anodic and Chemical Conversion Coatings on Aluminum and Magnesium Alloys
B08.08: Engineering Coatings
B08.09: Precious Metal Coatings
B08.10: General Test Methods
WG.01: Measurement of Coating Thickness, Chairman
B08.11: Government Specifications, Chairman
B08.20: Technical Advisory Groups to ISO/TC 107

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- B08.02: Substrate Preparation
- B08.03: Decorative Copper, Nickel, Chromium, and Nickel-Chromium Coatings
  - WG: Electrodeposited and Electroless Black Coatings for Solar Use
- B08.08: Engineering Coatings
- B08.10: General Test Methods

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- C5.02: Nomenclature, Units, & Editorial Matters, Chairman
- C5.05: Nuclear Applications
- C5.06: Executive Subcommittee

C8: Refractories Committee, S. J. Schneider, Member

D2: Petroleum Products and Lubricants
S. M. Hsu, Member:
- B-1: Passenger Car Oils
- P-1: Automotive Lubricants
- P-IV: Hydraulic Oils
- P-V: Industrial Oils
- T-B: Automotive Lubricants
- T-B-II: Heavy Duty Engine Oils
- T-Jt.8/P: Basestock Characterization
- T-P: Recycled Petroleum
- T-P-II: Used Oils and Basestocks
- T-P-III: Fuel Oils
- RDD-II: Elemental Analysis
- RDD-IV: Flow Properties
- RDD-IX: Oxidation
- T-L: Industrial Lubricants
- L-XI: General Functional, Chemical Tests
- L-XI-1: Falex Study Group
- L-XI-2: Four Ball Study Group
- L-XI-8: Coefficient of Friction Tests Study Group
- T-N: Hydraulic Oils
- N-II-1: Oxidation Study Group

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R. Gates, Member:
- T-L: Industrial Lubricants

J. J. Comeford, Member:
- D-2: Petroleum Products and Lubricants
- T-E-I: Burner Fuel Oils
- RDD-IV: Hydrocarbon Analysis
- RDD-IV-F: Absorption Spectroscopy Methods
- T-P: Recycled Petroleum Products and Lubricants, Advisory, Vice-Chairman
- T-P-I: Automotive Lubricants
- T-P-II: Used Oils and Base Stocks

T-P-III: Fuel Oils, Chairman
T-P-IV: Industrial and Hydraulic Oils
T-P-VI: Miscellaneous Products
T-P-VII: Editorial
RDD-IX-F: Used Oils Oxidation-Nitration

A. L. Cummings, Member:
RDD-III-A: Chemical Methods
RDD-III-C: Electrometric Method
RDD-VI: Analysis of Lubricants
RDD-VI-A: Chemical Analysis
RDD-Jt.API/ASTM: Water and Sediment
RDD-VII: Flow Properties

P. T. S. Pei, Member:
RDD-III: Elemental Analysis
RDD-III-A: Chemical Methods
RDD-IV: Hydrocarbon Analysis
RDD-IV-A: Chemical Analysis
RDD-IV-C: Liquid Phase Chromatography
RDD-VI: Analysis of Lubricants

S. J. Weeks, Member:
T-P: Recycled Petroleum Products
RDD-III: Elemental Analysis
RDD-IV: Hydrocarbon Analysis
RDD-VII: Flow Properties

E13: Molecular Spectroscopy
R. B. Johannesen, Member:
E13.07: Nuclear Magnetic Resonance, Chairman

E20: Temperature Committee
S. J. Schneider, Member

E34: Occupational Health and Safety Aspects of Materials, Physical and Biological Agents
F. E. Brinckman, Member:
E34.10: Definitions and Nomenclature

E47: Biological Effect and Environmental Fate
F. E. Brinckman, Member

G01: Corrosion of Metals
U. Bertocci, Member:
G01.11: Electrochemical Measurements in Corrosion Testing

E. Escalante, Member:
G01.10: Corrosion in Soils, Chairman

W. F. Gerhold, Member:

G01.01:	Research
G01.04:	Atmospheric Corrosion
G01.05:	Laboratory Corrosion Tests
G01.06:	Stress Corrosion Cracking and Corrosion Fatique
G01.98:	Advisory Committee on Exposure Test Facilities

W. P. Iverson, Member:

G01.10:	Corrosion in Soils TG: Electrochemical Polarization Techniques for Measurement of Corrosion Rates in Soils, Chairman

J. Kruger, Member:

G01.02:	Nomenclature
G01.90:	Executive Committee
G01.99:	Standing Committee on Liaison, Chairman

E. N. Pugh, Member:

G01.06:	Stress Corrosion Cracking and Corrosion Fatique
G01.06.05:	Section on Dynamic Testing, Chairman

Controlled Release Society (International)
Publications Committee
F. E. Brinckman, Member

Electrochemical Society
Nominating Committee
J. Kruger, Member

Editorial Committee
J. Kruger, Member
U. Bertocci, Member

Technical Affairs Committee
J. Kruger, Member

Corrosion Monograph Series Committee
J. Kruger, Member

Federation of Materials Societies
Long-Range Planning Committee
J. Kruger, Member,
Board of Trustees

Gordon Research Conferences
Council
J. Kruger, Member

High Temperature Science and Energy Technology
Editorial Advisory Board
J. W. Hastie, Member

International Committee for the Characterization & Terminology of Carbon
W. S. Horton, Vice Chairman

Interamerican Conferences on Materials Technology
Executive Committee
S. J. Schneider, Member

International Corrosion Council
J. Kruger, Member & U. S. Delegate

International Standards Organization
TC107: Metallic and Other Non-organic Coatings
F. Ogburn, Delegate:
1: Terminology, Delegate
2: Methods of Inspection and Coordination of Test Methods, Delegate
3: Electrodeposited Coatings and Related Finishes, Delegate
7: Corrosion Tests, Delegate

TC156: Corrosion of Metals
J. Kruger, Delegate
1: Terminology, Delegate

International Union of Pure and Applied Chemistry
II: Inorganic Chemistry Division
Division Committee
W. S. Horton, Member

Commission II-2: Nomenclature of Inorganic Chemistry
T. D. Coyle, Titular Member, Secretary

Commission II-3: High Temperatures and Refractory Materials
W. S. Horton, Associate Member
Subcommission II-3.1: Characterization and Terminology of Carbon, Co-Chairman

IUPAC Conferences on Refractories for Energy Applications
Planning and Program Committees
S. J. Schneider, Member

Joint Committee of Atomic and Molecular Physical Data
NMR Subcommittee
R. B. Johannesen, Chairman

Keramos (Ceramic National Fraternity)
S. J. Schneider, Member

The Metallurgical Society of AIME
Corrosion Resistant Metals Committee
E. N. Pugh, Member

National Bureau of Standards
Handicapped Advisory Committee
E. J. Parks, Chairman

National Institute of Ceramic Engineers
S. J. Schneider, Member

National Association of Corrosion Engineers
International Relations Committee
J. Kruger, Liaison Member

Government Affairs Committee
J. Kruger, Liaison Member

Publications Committee
J. Kruger, Member

Technical Practices Committee
J. Kruger, Member

Standing Committee on Technology Assessment
J. Kruger, Chairman

T10: Underground Corrosion Control
E. Escalante, Member

T3: Corrosion Science and Technology
W. P. Iverson, Member
T3L: Electrochemical and Electrical Techniques for Corrosion Measurement and Control

J. Kruger, Member
SC.B: Corrosion Products

National Research Council
Committee on High Temperature Science and Technology
J. W. Hastie, Member

National Materials Advisory Board
Committee on Environmentally Assisted Cracking Test: Methods for High Strength Steel Weldments
J. Kruger, Member
E. N. Pugh, Liaison Representative

Committee on Thermal Spray Coatings for Corrosion Control
D. S. Lashmore, Liaison Representative

Committee on Radioactive Waste Management
Subcommittee on Review of Swedish KBS-2 Plan
J. Kruger, Member
U. Bertocci, Consultant

National Science Foundation
Faculty Research Participation Program
F. E. Brinckman, Panel Chairman

U.S./U.S.S.R. Study Group on Corrosion
J. Kruger, Member
Passivity and Electrochemistry Project Coordinator

U.S./U.S.S.R. Cooperative Program on MHD
S. J. Schneider, Steering Committee

Publications

Applications of a Low Noise Potentiostat in Electrochemical Measurements
U. Bertocci
J. Electrochem. Soc. 127, 1931 (1980)

Studies on the Passive Film Breakdown by Detection and Analysis of Electrochemical Noise
U. Bertocci and J. Kruger
Surface Science 101, 608 (1980)
also Proc. Internat. Symp. on Non-Traditional Approaches to the Study of the Solid-Electrolyte Interface, North-Holland, Amsterdam, p. 608 (1980)

Determination of True Polarization Curves for Corrosion Rate Measurements of Steel in Stagnant NaCl Solutions
S. Wolynec and E. Escalante
Corrosion 36, 327 (1980)

Preferential Ordering of Mn and Fe Atomis in $Y_6(Fe_{1-x}Mn_x)_{23}$
V. K. Hardman, W. J. James, and W. E. Yelon
J. Phys. Chem. Solids 41, 1105 (1980)

Structural Investigations of $Th_6Mn_{23}D_{16}$ by Neutron Diffraction
V. K. Hardman, J. J. Rhyne, K. Smith, and W. E. Wallace
J. Less Common Metals 74, 97 (1980)

Possibilities for Application of Fundamental Approaches to Technological Problems
J. Kruger
Surface Science 101, 602 (1980)

Studies of the Orientation of Fracture Surfaces Produced in Austenitic Stainless Steels by Stress-Corrosion Cracking and Hydrogen Embrittlement
R. Liu, N. Narita, C. J. Altstetter, H. K. Birnbaum, and E. N. Pugh
Metall. Trans. 11A, 1563 (1980)

A New Ellipsometric-Electrochemical Approach to the Study of Corrosion Under Organic Coatings
J. J. Ritter and J. Kruger
Preprints of Symposium on Advances in Coating Metals for Corrosion Protection
Div. of Polymer Chem., Amer. Chem. Soc. 43, 575 (1980)

A Qualitative Ellipsometric-Electrochemical Approach to the Study of Film Growth Under Organic Coatings
J. J. Ritter and J. Kruger
Surface Science 96, 364 (1980)

Reactions of Benzyl Ions with Alkanes, Alkenes, and Aromatic Compounds
P. Ausloos, J. A. Jackson, and S. G. Lias
Int. J. Mass Spectrom. Ion Phys. 33, 269 (1980)

Dissimilatory Bacterial Sulfate Reduction in Southeastern Montana Groundwaters
W. S. Dockins, G. J. Olson, S. C. Turbak, and G. A. McFeters
Geomicrobiol. J. 2, 83 (1980)

Terminal Processes in the Anaerobic Degradation of an Algal-Bactaerial Mat in a High-Sulfate Hot Spring
D. M. Ward and G. J. Olson
Appl. Environ. Microbiol. 40, 67 (1980)

Engine Oil Evaluation Through Bench Testing
S. M. Hsu
Proc. Joint Conf. on Measurements and Standards for Recycled Oil/Systems Performance and Durability
NBS Spec. Pub. 584 (1980)

Characterization of Lubricating Basestocks
S. M. Hsu
Proc. Joint Conf. on Measurements and Standards for Recycled Oil/Systems Performance and Durability
NBS Spec. Pub. 584 (1980)

The Four-Ball Wear Test for Engine Oil Evaluation
S. M. Hsu and R. S. Gates
Proc. Joint Conf. on Measurements and Standards for Recycled Oil/Systems Performance and Durability
NBS Spec. Pub. 584 (1980)

Characterization of Re-refined Lubricating Base Oils
S. M. Hsu and D. A. Becker
SAE Technical Paper Series, #80132 (1980)

Laser-Excited Atomic Fluorescence Spectrometry
S. J. Weeks and J. D. Winefordner
Lasers in Chemical Analysis, G. M. Hieftie, J. C. Travis, and F. E. Lytle, eds., Humana Press, Clifton, New Jersey, Chapter 8 (1981)

Lasers and Analytical Polarimetry
A. L. Cummings, H. P. Layer, and R. J. Hocken
Lasers in Chemical Analysis, G. M. Hieftie, J. C. Travis, and F. E. Lytle, eds., Humana Press, Clifton, New Jersey, Chapter 15 (1981)

Temperature Profiles of Inhibited Flames Using Raman Spectroscopy
M. Drake and J. W. Hastie
Combustion and Flame 40, 201 (1981)

Volatilization of Mercury by Thiobacillus ferrooxidans
G. J. Olson, W. P. Iverson, and F. E. Brinckman
Current Microbiol. 5, 115 (1981)

Occurrence and Activity of Iron- and Sulfur-Oxidizing Microorganisms in Alkaline Coal Strip Mine Spils
G. J. Olson, G. A. McFeters, and K. L. Temple
Microbiol Ecology 7, 39 (1981)

The Effect of Calcium Carbonate on the Stability of Acid-Treated Papers
E. L. Graminski and E. J. Parks
J. Res. NBS 86, 309 (1981)

Separation Between Deterministic Response and Random Fluctuations by Means of the Cross-Power Spectrum in the Study of Electrochemical Noise
U. Bertocci
J. Electrochem. Soc. 128, 520 (1981)

Effect of Large Voltage Modulations on Electrodes Under Charge-Transfer Control
U. Bertocci and J. L. Mullen
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ASTM Tech. Pub. 727, p. 365 (1981)

Magnetic Structures of $Y_6(Fe_{1-x}Mn_x)_{23}$
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D. S. Lashmore
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Proc. Internat. Conf. on Heavy Metals in the Environment, Amsterdam (1981), in press

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High Temperature Science, in press

Flame Boundary Layer Effects in Line-of-Sight Optical Measurements
L. H. Grabner and J. W. Hastie
Combustion and Flame, in press

The Collection of Ions Produced by Laser-Enhanced Ionization in a Hydrogen/Air Flame
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Alkali Vapor Transport in Coal Conversion and Combustion Systems
J. W. Hastie, E. R. Plante, and D. W. Bonnell
ACS Symposium Series, in press

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D. W. Bonnell, A. J. Valerja, and J. L. Margrave
High Temperature Science, in press

Mass Spectrometric Studies of MHD Seed-Slag Thermochemistry
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Gas Chromatographic Speciation of Methylstannanes in the Chesapeake Bay Using Purge and Trap Sampling with a Tin-Selective Detector
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Fingerprinting Inorganic Arsenic and Organoarsenic Compounds in In Situ Oil Shale Process Waters Using a Liquid Chromatograph Coupled with an Atomic Absorption Spectrometer as a Detector
R. H. Fish, F. E. Brinckman, and K. L. Jewett
Environ. Sci. Technol., submitted

Vaporization Thermodynamics of K_2SO_4
E. R. Plante, T. Negas, and C. Olson
High Temperature Science, submitted

Laser Enhanced Ionization Flame Velocimeter
P. K. Schenck, J. C. Travis, G. C. Turk, and T. C. O'Haver
Applied Spectroscopy, submitted

Alkali Vapor Transport in the Na_2SO_4-H_2O System
D. W. Bonnell, D. M. Sanders, and J. W. Hastie
High Temperature Science, submitted

Atmospheric Effects on Vaporization Losses During Glass Melting
D. M. Sanders, D. W. Bonnell, J. W. Hastie, and W. K. Haller
Glass Technology, submitted

Division Seminars

The Division Seminar program has endeavored to arrange two talks each month; one by a speaker within the Bureau and a second by a speaker from outside. Responsibility for providing speakers rotates among the group leaders. It has not been possible to follow the idealized schedule exactly; however, we have had 24 talks scheduled in FY81, of whom all but three were speakers from outside. A chronological list of talks follows.

"Microbial Transformations of Metals"
H. L. Ehrlich
Department of Biology, Rensselaer Polytechnic Institute, Troy, New York
October 8, 1980

"Two-Dimensional Nucleation and Growth of Silver Electrodeposits"
R. Wiart
Associé à l'Université Pierre et Marie Curie, Paris, France
October 15, 1980

"Processes in Localized Corrosion"
H. Isaacs
Brookhaven National Laboratory, Upton, New York
October 16, 1980

"Wetting and Flow of Liquids Through Fabrics"
D. Clark
George Washington University Medical School, Washington, D.C.
October 17, 1980

"The Role of Oxide Films and Carbon in the SCC of Mild Steel"
J. Flis
Institute of Physical Chemistry, Warsaw, Poland
October 20, 1980

"Sulfur Ligand Chemistry of Tin"
R. C. Mehrotra
University of Delhi, Delhi, India
October 24, 1980

"In Situ Characterization of the Metal-Electrolyte Interface by Surface Enhanced Raman Spectroscopy"
M. Janik-Czachor
Institute of Sciences, Polish Academy of Sciences, Poland
November 3, 1980

"Highlights of Materials Research and Development in Breeder Reactor Technology"
P. C. S. Wu
U.S. Nuclear Regulatory Commission, Washington, D.C.
November 20, 1980

"Optogalvanic Spectroscopy"
P. W. Schenck
National Bureau of Standards, Washington, D.C.
December 8, 1980

"The Influence of Partial Elastohydrodynamic Lubrication on Surface Fatigue, Scuffing, and Wear"
H. S. Cheng, Northwestern University, Evanston, Illinois
January 25, 1981

"Corrosion Resistant Canisters for Nuclear Waste Isolation"
N. J. Magnani, Sandia National Laboratory, Albuquerque, New Mexico
February 9, 1981

"Electrochemical and Corrosion Studies on PbTe and HgPbTe"
H.-H. Strehblow
Institute of Physical Chemistry, University of Dusseldorf, Germany
March 30, 1981

"Vaporization of Potassia Containing Substances and Its Applicaton to MHD"
E. R. Plante
National Bureau of Standards, Washington, D.C.
April 16, 1981

"Properties of Electrodeposited Composite Coatings"
J. Zahavi
International Business Machines Corp., Poughkeepsie, New York
April 23, 1981

"Review of a Mathematical Model of Adhesive Wear and Its Control by Lubricants"
C. N. Rowe
Mobil Research and Development Corp., Paulsboro, New Jersey
April 24, 1981

"Time Evolution of the Depleted Atom Density Following Laser Enhanced Ionization in a Flame"
P. K. Schenck
National Bureau of Standards, Washington, D.C.
April 27, 1981

"Recent Studies in Polyanion Chemistry"
Y. Jeannin
Université Pierre et Marie Curie, Paris, France
May 8, 1981

"Electrocatalytic Effects on Underpotential Metal Electrodes"
K. Jüttner
Institute of Physical Chemistry, University of Karlsruhe, Germany
May 20, 1981

"Maximum Utilization Current Density and Cathodic Protection"
J. D. Talati
U.P. Arts College and Smt. M.G. Panchal Science College, Pilvai, India
May 26, 1981

"Controlled Release Antifouling Research"
V. J. Castelli
U.S. Naval Ship Research and Development Center, Annapolis, Maryland
June 9, 1981

"Mechanisms of Rapid Stress-Corrosion Crack Propagation in Brass and Sensitized Stainless Steels
R. C. Newman
Department of Nuclear Energy, Brookhaven National Laboratory, Upton, New York
July 28, 1981

"Fourier Transform NMR Studies of Organotins"
T. N. Mitchell
Department of Chemistry, University of Dortmund, Germany
July 30, 1981

"Formation of Calcareous Deposits in Synthetic and Natural Sea Water"
A. E. Yaniv
Lawrence Berkeley Laboratory, University of California, Berkeley,
August 27, 1981

"Compounds with Direct Phosphorus-Phosphorus Bonds"
H. C. E. Fluck
Gmelin-Institute, Germany
September 1, 1981

"Tubercle Characteristics in Water Distribution Systems"
O. H. Tuovinen
Department of Microbiology, Ohio State University
September 24, 1981

"New Inorganic Compounds with Heteronuclear Metal-Metal Bonds"
F. G. A. Stone
School of Chemistry, University of Bristol, England
September 28, 1981

External Recognition

J. A. Jackson
Washington Academy of Sciences
Fellow
February 1981

W. R. Blair
International Agricultural Centre Fellowship
Netherlands Ministry of Agriculture
Institute of Soil Fertility, Groningen
May-October 1981

F. E. Brinckman
Main Session Chairman; Panel Discussion Chairman
Fifth International Symposium on Environmental Biogeochemistry
Stockholm, Sweden
June 1981

W. P. Iverson and F. E. Brinckman, Co-Managers
NSF Industrial Research Participation Program Host Laboratory
Transformations of Metal-Containing Materials in the Environment
1981-1982

Books

Electrochemical Corrosion Testing
F. Mansfield and U. Bertocci, eds.
ASTM Special Technical Publication, 1981

Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes
F. E. Brinckman and R. H. Fish, eds.
Proc. of DOE/NBS Workshop on Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes
May 18-20, 1981
NBS Special Publication 618, ca. 300 pages, 1981, in preparation (camera-ready)

Special Reports

Passive Films, Surface Structure and Stress Corrosion, and Crevice Corrosion Susceptibility
J. Kruger, J. J. Ritter, J. J. Carroll, and A. J. Melmed
NBSIR 80-2101 (Report to the Office of Naval Research)
Technical Summary Report No. 10 (August 1980)

Speciation of Inorganic and Organic Arsenic Compounds in Oil Shale Process Waters
R. H. Fish, J. P. Fox, F. E. Brinckman, and K. L. Jewett
Energy & Environment Div., Lawrence Berkeley Laboratory Annual Report 1979
LBL-11650
October 1980

Plating on Aluminum
D. S. Lashmore
NBSIR 81-2191 (Report to the Aluminum Association)
November 1980

Vaporization and Chemical Transport in Coal Gasification
J. W. Hastie, D. W. Bonnell, E. R. Plante, and W. S. Horton
NBSIR 80-2178 (Report to Department of Energy)
December 1980

Use of the Slow Strain Rate Technique for the Evluation of Structural Materials for Application in High Temperature Gaseous Environments
G. M. Ugiansky and C. E. Johnson
NBSIR 81-2191 (Report to Department of Energy)
January 1981

The Corrosion Behavior of Selected Stainless Steels in Soil Environments
W. F. Gerhold, E. Escalante, and B. T. Sanderson
NBSIR 81-2228 (Report to American Iron and Steel Institute)
February 1981

Corrosion Evaluation of Underground Telephone Cable Shielding Materials
W. F. Gerhold and J. L. Fink
NBSIR 81-2243 (Progress Report for Rural Electrification Administration)
Progress Report 1976-1980
April 1981

Biodeterioration of Standard Reference Materials
G. J. Olson, W. P. Iverson, and F. E. Brinckman
NBSIR 81-2246 (Report for Office of Standard Reference Materials)
April 1981

Alkali Vapor Transport in Coal Conversion and Combustion Systems
J. . Hastie, E. R. Plante, and D. W. Bonnell
NBSIR 81-2127
May 1981

Mass Spectrometric Studies of MHD Seed-Slag Thermochemistry
J. W. Hastie and E. R. Plante
NBSIR 81-2293
June 1981

NBS: MATERIALS RESEARCH
Ed., J. R. Manning
Measurement of High Temperature Thermophysical Properties of Tungsten Liquid and Solid (60-87)
D. W. Bonnell
NBSIR 81-2295 (Annual Report to NASA)
June 1981

Materials for Instrumentation in Coal Conversion
H. P. R. Frederikse, P. K. Schenck, G. Burns, R. Dils, and J. Whetstone
NBSIR (Report to Department of Energy), in press

Passive Films, Surface Structure and Stress Corrosion, and Crevice Corrosion Susceptibility
J. Kruger, J. J. Ritter, J. J. Carroll, and A. J. Melmed
Tech. Summary Report No. 11, in press

Standard Reference Materials

The Division produces coating thickness SRMs, used to calibtate coating thickness gauges. A single SRM is a metal coupon, 3 x 3 cm or 1.5 x 1.5 cm, one surface of which has a nelectroplated coating of certified thickness. Most of these are non-magnetic coatings on steel, but also included are nickel, gold, and tin coatings on various metallic substrates. Some 53 different SRMs are made ranging in thickness from 0.7 μm to 2 mm. (Gold coatings are actually certified in units of mass/area, not length.) They are designed for use with either magnetic type of beta backscatter type thickness gauges.

These SRMs are packaged in sets and the SRM catalog lists some 31 different sets. About 5000 individual coating thickness standards were produced during FY80 and about 4700 were produced during FY81. The Division produced and delivered 100 Penetrant Test Block SRMs. This new SRM contains four cracks of known widths and is used to check the sensitivity of liquid dye penetrants and of dye penetrant systems. The nominal widths of the four cracks are 0.2, 0.5, 1.0, and 2.0 μm.

Patent

U.S. Patent 4,233,107
Ultra-black Coating Due to Surface Morphology
C. E. Johnson
November 11, 1980

Sponsored Conferences

DOE/NBS Workshop on Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy-Related Processes
National Bureau of Standards, Washington, D.C.
May 18-20, 1981
F. E. Brinckman, Co-Chairman

Fifth Annual Conference on Materials for Coal Conversion and Utilization
National Bureau of Standards, Washington, D.C.
October 1981
S. J. Schneider

FRACTURE AND DEFORMATION DIVISION

FRACTURE AND DEFORMATION DIVISION

Richard P. Reed, Chief
Sheldon M. Wiederhorn, Deputy Chief
D. C. Shields, Administrative Officer
P. L. Salpino, Administrative Assistant
C. J. Montgomery, Secretary
D. L. Mills, Secretary

Structures and components must be mechanically reliable. A significantly large portion of our Nation's effort to ensure public safety and environmental quality concentrates on materials and structural mechanical integrity. Material fracture imposes a high cost on the national economy. Careful design, structural codes and standards, material development and characterization, quality control and inspection, and the replacement, inconvenience, injuries, and deaths from unexpected failures all contribute to this cost.

The Division is currently assessing the costs of fracture to the Nation. This study was mandated by the Subcommittees on Natural Resources and Environment and on Science, Research, and Technology of the House of Representatives Committee on Science and Technology. Even with the use of the currently best available design, fabrication, and inspection procedures, it sometimes happens that structures, mechanical components, and containers fail during use. The economic consequences for the domestic economy of unintended failures and the costs to prevent fracture are large. The documentation of these costs is one purpose of this study. A second purpose is to determine the economic benefits to be derived from wider application of existing fracture-control technology. The third purpose is to establish the economic impact of the utilization of improved understanding of fracture processes and the control of fracture and to identify the most important research areas.

The principal goal of the Fracture and Deformation Division is to minimize material failure. There are three essential research thrusts to improve material mechanical performance:

1. Theory and modeling of deformation and fracture lead to a fundamental understanding of the mechanisms of material mechanical response.

2. Characterization of mechanical performance is essential for the proper development and selection of materials for service applications and for efficient design that takes full advantage of the performance.

3. Fracture-mechanics development and application provide quantitative assessment and standards for the integrity of critical structures by relating material properties to flaw characterization and service environment.

The research of the Fracture and Deformation Division emphasizes the critical areas of these three thrusts. These critical areas, subsequently referred to as Tasks, are discussed in this report.

Division personnel are located in both Boulder and Gaithersburg. Although separate geographically, these two groups complement each other. The Boulder group emphasizes elastic-plastic fracture mechanics and low-temperature properties in its study of metals, alloys, and composites. The Gaithersburg group emphasizes time-dependent deformation and fracture mechanisms, high-temperature properties of metals and alloys, and mechanical properties of ceramics. Together these groups represent much of the expertise in mechanical properties and in fracture mechanics at NBS.

The technical outputs of the Division assist many Government agencies, including the National Aeronautics and Space Administration and the Departments of Energy, Transportation, and Defense. Recent emphasis on fusion, coal conversion, and geothermal energy by the Department of Energy has led to several efforts: low-temperature research for structural containment of the large magnetic fields produced by superconducting magnets, property characterization of geothermal cements, study of high-temperature deformation and crack growth of coal-conversion-system structural ceramics, and the preparation of a handbook on coal conversion systems material performance. Transportation-related research includes establishing inspection and allowable-defect-size standards for pipeline girth welds, mechanical-property and microstructural characterization of pressure-tank-car steels and railroad wheels, fracture-mechanics assessment of tank-car behavior, development of test standards for lightweight compressed gas cylinders, and numerous structural metal-fracture analyses. Research for the Department of Defense is diverse. We are assisting the Navy in upgrading their fracture-control plans, identifying material limitations in ultrasensitive inertial-guidance-system gyroscopes, studying the applicability of proof testing to nitride and carbide ceramics that may be used in gas-turbine engines, conducting erosion and wear experiments of ceramics to reduce machining costs, and studying the fracture and elastic characteristics of new silicon-carbide, aluminum-based composites. The creep, fracture toughness, strength, and elastic properties of several alkali halides are being studied to assist NASA in proper selection of the scintillation material for the NASA Gamma Ray Laboratory.

The Division hosts and leads a number of workshops and conferences each year. Collaborating with the DOE, annual workshops on "Materials at Low Temperatures" are hosted each year. The Mechanical Failure Prevention Group hosted two conferences: "Detection, Diagnosis, and Prognosis Contributions to the Energy Challenge" and "Innovation for Maintenance Technology Improvements." With the British Welding Institute and the American Welding Society, our Division has planned a 1982 conference on "Fitness-for-Service." The Division actively leads and supports the International Cryogenic Materials Conference, which held its annual meeting in San Diego, California.

New opportunities for research have been provided in the Division by the NBS Durability Program. Increased emphasis has been placed on elastic-plastic fracture mechanics. Workmanship codes need to be extended to fitness-for-service alternatives to reduce repair welds, to assess specific defects in critical structures, to formulate fracture-control plans for critical structures, and to estimate structural-integrity lifetimes. Elastic-plastic fracture-mechanics models and methodologies are needed to replace the traditional linear-elastic fracture-mechanics approach because most structural alloys for critical applications are selected to ensure against crack instability preceding plastic

deformation. Therefore, research has been initiated on test methodologies, model development and verification, and effects of defects and subcritical crack growth; all of these relate to elastic-plastic or all-plastic conditions.

New studies have also been started on high-temperature or time-dependent properties of metals. Such research is timely because new energy-conversion systems, plasma-containment systems, and nuclear systems all have serious material-selection and durability problems associated with understanding and characterizing the time-dependent fracture processes in structural alloys. Study of crack-tip fracture mechanisms, characterization of fracture processes, and generation of property data (emphasizing creep and fatigue), will provide new insights to assist in high-temperature design and material selection.

Three principal research tasks have been established to emphasize the research directions of our Division:

12121	FRACTURE MECHANISMS AND ANALYSES
12122	DURABILITY OF CERAMICS AND COMPOSITES
12123	ELASTIC-PLASTIC FRACTURE MECHANICS

Research within our Division is discussed under subtasks of these three tasks. Tasks 1 and 3 have received greater emphasis under the Materials Durability Program, and Task 2 emphasizes research directed toward mechanical behavior of high performance ceramics and composites.

FRACTURE MECHANISMS AND ANALYSES
Task 12121

For structural materials, a knowledge of the basics of crack-tip processes is essential to understanding fracture in these materials and to predicting their long-term service life. Influences of atomic structure and chemical reactions at crack-tips have been demonstrated with atomistic models of fracture in a solid, but these influences have not yet been confirmed quantitatively by experimental studies of subcritical crack growth and environmental effects. Ductile processes in the high-stress region of the crack tip must be introduced into these atomistic models to assess the role of plastic deformation and to extend the theoretical models to describe crack-growth phenomena such as fatigue. High-temperature fracture is a complex process with competitive fracture mechanisms, such as subcritical crack growth, cavity nucleation and growth, and grain-boundary sliding; it is affected by microstructure, impurity content and segregation, processing history, and environment.

Failure analysis studies perform a valuable service for those Government agencies that have no testing facilities and require research on the safety of structural materials. By using modern metallographic, x-ray, fractographic, and chemical analyses techniques and maintaining a Failure Information Center, our Division serves as a focal point for analyses and compilation of many critical structural failures.

Our Division program on fracture mechanisms and failure analyses has as its objectives a broad spectrum of goals: (1) the development of fundamental theories on crack-tip processes, (2) the generation of data to elucidate these crack-tip mechanisms, (3) the development of fracture methodologies for predicting structural reliability, and (4) the application of established methodologies in the analysis of actual failures. In addition, the NBS Materials Durability Program has provided funding for increased emphasis on high-temperature fracture processes and mechanisms. Our understanding of the fracture of metals under time-dependent conditions will be increased by research on crack-tip theory coupled with high-temperature tensile, creep, and fatigue properties.

Fracture Theory
Subtask 1 of Task 12121

T.-J. Chuang, R. deWit, R. J. Fields, E. R. Fuller, Jr., C. G. Interrante, M. B. Kasen, R. M. Thomson

Predictions of crack growth and fracture and, hence, of component reliability can only be attained rationally through a fundamental understanding of crack-tip structures and crack-tip processes. In this subtask, theories are being developed to study these fracture mechanisms.

Lattice Theories of Fracture. The desire for understanding at a fundamental level has provided considerable impetus to atomistic modeling of cracks and crack-tip processes. Considering a one-dimensional lattice model of a crack, the nonlinear interatomic interactions in the crack-tip region can be effectively decoupled from the linear elastic interactions in the bulk solid. Using this stratagem, a phenomenological mechanics model has been developed within which the influence of the crack-tip-bond interaction can be explored, whether that interaction is intrinsic or chemically effected.

An important result from this model is a derivation of a general form of the stress-intensity factor dependence of the activation volume and the activation energy for crack propagation. Utilizing a Green's function approach and the method of lattice statics, this analysis has been extended to more realistic crack configurations in two- and three-dimensional cubic lattices. The concept of partitioning the fracture phenomenon into two parts, one specific to the crack-tip region and another specific to the bulk elastic solid, remains as a general feature in these more realistic configurations.

Grain-Boundary Chemistry and Structure. Crack tip structures and crack tip processes are strongly influenced by localized variations in chemistry. The predominant factor influencing such variations is microsegregation; in particular, segregation to grain boundaries. Although models based on thermodynamic equilibrium or vacancy-solute coupling have been proposed to account for observed segregate levels, their range of applicability has been limited. During the past year, an analysis of data from an NBS study of solute redistribution during grain growth has defined a mechanism of segregation in which grain boundary motion plays a dominant role. This analysis has given rise to development of a general theory of segregation applicable to all metallic systems and incorporating the ability to predict changing segregate levels from the solute-free boundary condition through full boundary saturation and to establish solute profiles and precipitate development. The theory predicts development of microsegregated regions in the interior of grains as well as at boundaries, consistent with the observation of both intergranular and transgranular failure modes. A unique aspect of the theory is the prediction of an athermal boundary structural change that is activated by attainment of full boundary solute saturation. The theory provides a method for a quantitative correlation between the level and species of segregate, fracture toughness, and crack growth rate. It also offers insight into the atomistic mechanisms operating at the crack tip.

Crack Tip Opening Displacement Model. A crack tip opening displacement (CTOD) model has been used to establish a correlation between fracture toughness and specimen-strength ratio and to analyze failure criteria for through-cracked vessels. This CTOD model is the Dugdale/Bilby-Cottrell-Swinden (D-BCS) model as extended to finite geometries and structures by Heald, Spink, and Worthington (HSW). Using the D-BCS-HSW model, the fracture toughness of a pressure vessel steel was correlated with the specimen strength ratio data reported by Server and Wullaert for various specimen configurations. This good correlation has the potential of replacing costly plane-strain fracture toughness tests with simpler, and less expensive, specimen-strength-ratio measurements. Because the D-BCS-HSW model embodies many features of a material's failure behavior from linear elastic fracture mechanics to plastic collapse, it also was used to evaluate several failure criteria for through-cracked vessels. The model presents a unified picture of these criteria and embodies many important features of the whole range of fracture mechanics. One such feature is exemplified in residual strength diagrams, where the model shows that for increasing fracture toughness, decreasing flow stress, or decreasing structure size, the concepts of linear-elastic fracture mechanics and, subsequently, elastic-plastic fracture mechanics disappear.

The model has also been applied in the ASTM "Predictive Round Robin on Fracture," where it successfully predicted the failure load of 76 different

specimens, including tensile, compact, and specially designed specimens, of two different aluminum alloys with different crack sizes and width dimensions. In the future, the model will be applied to analyze pressure vessel failures as part of a study on railroad tank-car failures.

Fracture Mechanics Concepts. A survey of fracture mechanics concepts and test methods is being prepared in collaboration with Prof. George R. Irwin of the University of Maryland. A summary of this survey was prepared this year; it presents concise definitions of the basic concepts of fracture mechanics, discusses various subcritical crack propagation mechanisms, and concludes with the concept of a fracture control plan.

Elevated-Temperature Fracture. At lower temperatures, time-dependent failure results primarily from chemically assisted subcritical crack growth. As the temperature increases, however, creep deformation and creep crack growth become important elements of high temperature failure processes. With the initiation of experimental studies in this area, we have begun to consider models of crack growth in a creeping material. When the creep behavior is localized to the crack-tip region, a strain-rate-dependent zone correction (analogous to the plastic zone correction used by Irwin for small-scale yielding) adequately describes the strain-rate dependence of the high temperature toughness. When the creep behavior is not localized, however, a more detailed account must be taken of the influence of time-dependent deformation on the fracture process. Currently, the parameter controlling the creep crack growth behavior in this region is thought to be the C* integral. In this regard, we are reviewing several recent manuscripts on this subject.

Diffusive Mechanisms of High Temperature Crack Growth. A study was conducted on diffusive mechanisms of crack growth along grain interfaces at elevated temperatures. Growth is assumed to occur by matter transport from the crack surfaces into the grain boundary under the influence of the applied stress. In contrast to the well-known Hull-Rimmer model, a Chuang-Rice crack-like cavity is considered to grow at steady state in an infinite bicrystal subject to a constant remote stress field. The grains on both sides of the crack are assumed to behave elastically. Gradients of the normal stress acting on the interface drive the grain boundary diffusion, whereas the stress itself is the sum of that due to the applied stress plus a residual stress due to nonuniform matter addition to the abutting grains by self-diffusion. The coupled effects of elastic deformation and atomic diffusion result in a singular integral equation for stress, which was solved and leads to an equation correlating applied stress to the crack-growth rate. This equation shows that a threshold stress exists below which the crack ceases to grow. Comparison of the theory with creep crack-growth data on Si-Al-O-N ceramics at 1673 °C shows good agreement.

The energy release rate associated with the crack growth was also studied in more detail. We found that the energy loss on crack advance is primarily due to the work done by the grain boundary normal stress on the opening displacement rather than the strain energy release of the adjoint grains.

Crack-Growth Mechanism Maps. Often our ability to assess a material's behavior in different environments and temperature regions depends as much on the form in which we present the engineering information as on the information itself. During the past two years, a different method of expressing crack-growth data

has been developed that clearly delineates mechanisms of crack growth as a function of temperature and stress-intensity factor. Contours of constant material response, namely, crack-growth rate, are plotted on a diagram of the experimentally controllable parameters: temperature and stress-intensity factor. This type of representation emphasizes changes in a material's fracture mechanism as either the temperature or the stress-intensity factor change, and thereby displays the variety of ways that cracks can grow in a material. We have used these crack-growth-mechanism maps as an aid in the critical evaluation of elevated-temperature crack growth and fracture data. They provide a broad and self-consistent picture of a material's resistance to crack growth and clearly indicate regions where data either are missing or are contradictory. These maps have been prepared for a number of materials, including a nickel-base superalloy, an aluminum alloy, a hot-pressed silicon nitride, a hot-pressed silicon carbide, and a number of silicate glasses. Some results of this work were presented at the Fifth International Conference on Fracture held March 29 to April 3, 1981, in Cannes, France, and were published as part of the proceedings of that conference. This work is jointly supported by Task 12121 and 12122.

Time-Dependent Fracture Processes
Subtask 2 of Task 12121

T.-J. Chuang, R. deWit, J. G. Early, R. J. Fields, S. W. Freiman, E. R. Fuller, Jr., G. E. Hicho, C. G. Interrante, R. S. Polvani, C. H. Brady, L. Chuck, D. E. Harne, S. R. Low, L. C. Smith

The objectives of this subtask are to investigate time-dependent fracture mechanisms and to improve test methods for two generic categories: (1) those fracture processes that are governed by environmental effects on a material under sustained loading conditions, and (2) those fracture processes that are influenced by a strain-rate sensitivity of the material. As a counterpart of these objectives, these methods are applied to significant materials problems.

Chemically Assisted Crack Growth. Crack-growth experiments are being conducted in controlled atmospheres to provide experimental corroboration with our atomistic theories of chemically assisted crack growth. An optimum selection of material, environment, and temperature is necessary to ensure chemical adsorption at the crack tip and yet to prevent complications that result from crack-tip dislocation processes. Accordingly, initial experiments have been directed toward characterizing the crack-growth behavior of a soda-lime-silicate glass and fused silica as a function of temperature in vacuum and in gaseous environments of argon and argon with two percent hydrogen. Since chemically assisted crack growth in this material is generally attributed to the presence of water vapor, these experiments will help to clarify the role, if any, of hydrogen. Further studies will be conducted on single-crystal silicon, a material that does not appear to exhibit any type of subcritical crack growth, and brittle metals.

Hydrogen Embrittlement of Steels. Another environmental study in the area of sustained load testing is that of hydrogen embrittlement of steels. As a result of past efforts, studies have been published on: (1) a method for measurement of the permeation of hydrogen in metals, (2) a method for removal

of iron sulfides from fracture surfaces that have been exposed to aqueous sulfide environments, and (3) studies of the effect of temper embrittlement of steel on the susceptibility of steel to hydrogen embrittlement.

Last year, attention was centered on completing work on development of an automated real-time method of analysis of crack-growth rates of steels tested in aggressive aqueous environments. This method has been applied to study the behavior of a 2.25 Cr - 1.0 Mo steel tested in an acetic solution containing H_2S at 0.1 MPa (1 atm) of pressure. A publication of the results of this work describes the apparatus and the measurement procedures developed in our laboratory and gives real-time crack-growth rates for this steel. These crack-growth rates were computed from dc electrical resistance measurements of crack length in double cantilever beam (DCB) type of fracture-mechanics test specimens--future studies will include measurements taken with a more sensitive ac electrical resistance system, as well as results of some thicker, compact-tension (CT) type specimens. Variables that will be included in future studies are tempering temperature for the 2.25 Cr - 1.0 Mo steel, specimen orientation with respect to rolling direction, and the partial pressure of H_2S in an aqueous acetic acid environment. In addition, work is continuing on the determination of conditions that promote the formation of branch cracks in DCB specimens tested in severe sulfide environments. These studies of hydrogen embrittlement problems have been conducted under the guidance of the Subcommittee on Hydrogen Embrittlement of the Pressure Vessel Research Committee of the Welding Research Council (WRC). Work on an interpretive report to be published as a WRC Bulletin is now in progress. This work will be titled "Effects of Hydrogen on Pressure Vessel Steels." NBS personnel are actively participating in and promoting an international conference on "Current Solutions to Hydrogen Problems in Steels," which is slated for November 1982 in Washington, D.C.

Creep-Assisted Crack Growth. Another area of time-dependent fracture response that we have begun to examine this year is creep-assisted crack growth at elevated temperatures. In our initial experiments, we are measuring sustained load crack growth in an aluminum alloy (2024-T6) at 423 K. Thus far, we have measured the time-to-failure as a function of initial stress intensity factor, and we are presently conducting interrupted tests to obtain the crack-growth rate behavior. Further experiments will be conducted on a harder material in a T851 heat treatment, and ultimately these techniques will be applied to high temperature crack growth in a high-chromium ferritic stainless steel.

Creep Rupture Processes. As part of our effort to characterize creep-assisted crack growth at elevated temperatures we have been studying high temperature creep cavitation and creep rupture processes. Initial experiments have examined the creep-cavitation behavior ahead of a growing crack in copper and in a high temperature structural alloy. Both center-cracked panels and single-edge-notched tensile specimens have been subjected to an applied load at elevated temperature to extend the crack by creep-crack growth. The distribution of cavities around the crack tip is then characterized using automated quantitative metallographic techniques. Further experimental research in this area will focus on measuring void nucleation and growth rates at grain boundaries in structural steels used in energy conversion systems. These studies will help to provide an understanding both of the creep cavitation behavior in the highly nonuniform stress field ahead of a crack and how these cavities contribute to the crack-growth process. Further studies will compare creep rupture predictions from

empirically derived models and from an inelastic finite-element analysis with experimental results obtained on notched specimens tested under sustained load creep conditions.

Fracture Under Impact Loading. Impact-test studies in our laboratory have centered on both the pendulum and drop-weight tests, which are used to measure the fracture toughness of metals and alloys at high strain rates. Results of these impact tests are often useful in fracture control, on the basis of either service experience or empirical correlations with fracture mechanics tests. Pendulum testing includes tests of both standard and the precracked Charpy V-notch (CVN) type specimens. Test-method-development activities for CVN testing have involved our participation in ASTM activities on the development of standard test methods for precracked CVN specimens. Results of our work will appear later this year in a publication on the significance of CVN precracking variables in determining test responses of precracked slow-bend test specimens. Drop-weight testing includes dynamic-tear (DT) tests and drop-weight NDT tests. Test-method-development activities have involved publication this year of a method for computer-assisted testing and data analysis for these impact tests. Future work will include results of analyses of several alternative methods for the measurement of energy absorption in DT and CVN tests. Applications in which impact testing has been used to serve Government agencies include works on plate materials used for railroad tank cars and in pipelines, as well as structural steels used in highway bridges.

Material Performance Center
Subtask 3 of Task 12121

B. W. Christ, H. Ondik, W. A. Willard

The Material Performance Center assists the coal conversion industry in extending the useful life and reliability of plant components by maintaining a central source of information on the performance, especially failures, of materials and components used in coal conversion environments. It provides an integrated material-properties data base for construction materials to aid in the design, construction, and operation of coal conversion plants. Finally, it collects and evaluates the information, maintains computer files for convenient retrieval, and disseminates the data in convenient form to users.

Sources of the information compiled by the Material Performance Center include operators of all gasification and liquefaction processes, from bench-scale units through operating pilot plants participating in the DOE voluntary failure reporting program. Information detail varies from one-page failure-occurrence reports to final reports of laboratory analyses of failed parts.

A computerized data base of approximately five hundred reported failures has been established and is continually being updated, refined, and increased as additional failure reports are received. Separate information items addressing the same failure are collated when possible. In addition, direct contact with operating personnel at the various process locations and with failure analysis laboratory staff has enhanced the quality and the flow of information and has assisted plant operators in problem solving.

At present, the Center produces sets of abstracts covering all reported incidents. The abstracts are intensive summaries constructed from the source document and they contain all reported data. They are sorted according to material, component type, failure mode, and conversion process, or any combination of these factors.

Although fewer pilot plants are now operating, resulting in a very slow rate of increase of the data file, there is continuing interest on the part of the user community. Some 16 reports, 70 statistical data tables, and approximately 5000 abstracts summarizing in-service materials and components performance were sent out in response to over two dozen requests. In addition, information is regularly supplied for the Failure Experiences feature of the DOE Materials and Components Newsletter, published by Battelle-Columbus Laboratories.

The major effort for the past year has been the preparation of a handbook Construction Materials for Coal Gasification--Performance and Properties Data. This book contains information gained in practical plant experience and the results of materials research and testing programs. It deals with the information in the context of eleven separate component areas of coal gasification plants and draws from this information an indication of possible candidate materials of construction. A separate section of the book includes extended data for the chemical, physical, and mechanical properties of the candidate materials. The book will consist of loose-leaf pages so that increasing and revising the data can be done readily on a regular basis.

Failure Avoidance Services
Subtask 4 of Task 12121

B. W. Christ, J. G. Early, G. E. Hicho, C. G. Interrante, T. R. Shives, J. H. Smith, W. A. Willard

Failure avoidance services provided to other Government agencies and other Divisions within NBS include diagnostic failure analysis, mechanical-properties testing, metallographic analysis, and metallurgical consultation. The results of this work have been used to assist in the develoment of safety regulations, in the selection of materials to improve the reliability of components and structures, and the development of improved test methods and standards. In many cases, diagnostic failure analysis of failed components has led to the identification of needed research in materials characterization, and this research is now part of the on-going programs described in this report. During the present year, eleven reports of specific projects in failure analysis and failure avoidance were completed. As in previous years, projects were completed for the National Transportation Safety Board, the Consumer Product Safety Commission, the Federal Railroad Administration, and the Office of Hazardous Materials. Also, special projects were completed for several other Federal agencies. Reports of these investigations are shown in the list of publications in this report.

A diagnostic failure investigation for the National Transportation Safety Board (NTSB) was completed on a section of failed gas pipeline. Results of this investigation are used by NTSB to identify potential hazards in transportation systems and to advise the Department of Transportation on the need for improved safety regulations.

Investigations for the Consumer Product Safety Commission (CPSC) included analysis of lawn mowers, hardware items, household electric heaters, and copper tubing. The results of these investigations are used by CPSC to assess the need for modifications to the design of materials used in these products to reduce the risk of injury to the public.

Recent investigations on several metallic components used for implantation during surgery have been completed for the Food and Drug Administration. Identification of the cause of premature failure in these components is essential to improving the reliability of these components.

A major investigation to identify the cause of cracking in welds in the replacement Silver Bridge at Point Pleasant, West Virginia, is being finalized for the Federal Highway Administration. The results of this investigation will be used by the FHA to specify materials requirements, welding procedures, and weld-repair procedures to be used in future bridge construction. Weld cracking has been identified as a problem in several large bridges recently constructed throughout the interstate highway system. Identification of the causes of these cracks and the specification of corrective measures is an urgent national problem.

Continuing work for the Federal Railroad Administration involves identification of the causes of failure in railway tank cars and wheels. For tank cars, the work involves considerations for fracture safe design and improved materials to resist fracture in the event of tank-car accidents. The extreme hazard resulting from frequent accidents involving tank cars containing hazardous materials is a national problem of growing significance. Results of the NBS work on tank-car materials have assisted in the development of specifications for new tank cars that will significantly reduce the frequency of major tank-car accidents.

Besides these major failure analysis investigations, a wide range of other projects was completed. Determination of the cause of failure in several types of fasteners was completed for the Coast Guard. Failure investigations were completed on failed piping and pressure vessels for the Materials Transportation Bureau (MTB) of the Department of Transportation. The results of these investigations are used by MTB to develop a data base on failure experiences in pressure vessels and piping and to determine if modifications to their safety regulation are required.

The dissemination of information to assist in Failure Avoidance was continued by the NBS sponsorship of two meetings of the Mechanical Failures Prevention Group (MFPG). A meeting with the theme "Detection, Diagnosis, and Prognosis--Contributions to the Energy Challenge," was held in October 1980 and emphasized the use of detection, diagnosis, and prognosis techniques in energy-related systems. The April 1981 meeting of the MFPG was on "Innovation for Maintenance Technology Improvements." The spring 1982 meeting of the MFPG will be organized by the Fracture and Deformation Division. The theme will focus on assessment methodology of failure, including decision-making based on the input data.

Plastic Deformation of Metals
Subtask 5 of Task 12121

B. W. Christ, R. J. Fields, E. R. Fuller, Jr., G. E. Hicho, R. S. Polvani

Microdeformation of Metals. Because of needs to design more dimensionally stable structures, for example, metrology fixtures and inertial guidance systems for naval application, tensile microcreep and microyield strength behavior are being measured for several metals and alloys, beryllium, and Super Invar. The overall goals of this study are: (1) to develop a data base--preferably in the form of a model--for creep strains of less than 10^{-8} and at rates of $10^{-15} s^{-1}$, and (2) to develop a fundamental understanding of the dislocation processes limiting these small strains. This program involves the combined efforts of two NBS groups along with researchers at the C. S. Draper Laboratory (Cambridge, Massachusetts) and Lawrence Livermore Laboratory (Livermore, California).

Microyield and microcreep testing have been conducted at temperatures between room temperature and 373 K, and at stresses between 50 kPa and 200 MPa. To detect strains with an accuracy of 10^{-7} strain, temperatures in two of our test frames are held to ± 0.01 degree over test intervals of several thousand hours. A third system, designed to detect strains in the 10^{-8} range, operates at temperatures below 313 K, but with a temperature stability of ± 0.0005 degree. Finally, a biaxial testing system was completed and is in use.

Testing methodology is being developed to promote better sample alignment, more accurate determinations of the instantaneous creep strain, and reduction of the test sample variability. Test results show that both metal alloys microcreep appreciably well below their microyield strengths. For example, the I-400 grade beryllium exhibits a strain of about 10^{-6} in 1000 h at a stress of 20 MPa (3000 psi). Additional features are that microcreep has a linear stress sensitivity, a strong temperature sensitivity, and the strain depends on the log of the time. Importantly, microcreep and microyield strengths are history sensitive, depending critically on the level of prestrain. Statistical aspects of fitting microcreep data to creep relationships are also being developed. Confidence limits for the nonlinear curve fit have been established that allow extrapolation of the microcreep strains to longer times.

Dynamic Hardness. Because of the importance of hardness to the nucleation of cracks and to other wear mechanisms during erosion, an attempt is being made to measure the dynamic hardness of metals and ceramics. This is a joint effort of Tasks 12121 and 12122. One approach taken to obtain a measure of dynamic hardness is to analyze the acoustic signals generated during impact event. These acoustic waves propagate from the impact source event, are received at a location remoted from the source, and can be analyzed so that an impact-load-time profile can be obtained for the real time impact situation. Modifications of an existing impact apparatus have been completed and impact profiles and velocities have been obtained for an aluminum alloy. Currently, the impact data are being coupled to a computer for efficient analysis. Experiments, conducted this year, will characterize the impact force as a function of velocity. The dynamic hardness as obtained using the impact/velocity data and that obtained from direct measurements will be compared. In addition

to these experiments, experiments will be conducted on large plates of soda-lime-silicate glass to obtain a reasonably accurate picture of the types of forces that are generated during solid particle erosion.

Strength Differential Effect. A research program was initiated this year to apply some of the unique techniques available at NBS to examine the strength differential effect. This effect is commonly observed in metals with a large yield stress to elastic modulus ratio, such as maraging steel. Although previous investigations have examined the strength differential effect and numerous explanations for the phenomenon have been proposed, only a few attempts have been made to correlate the effect with microstructural modifications of the material. The present research program will critically examine some of these explanations through the use of various high resolution techniques at NBS, namely, high-precision density measurements, small-angle neutron scattering, and scanning transmission electron microscopy. This program is a joint effort of the Fracture and Deformation Division and the Metallurgy Division.

DURABILITY OF CERAMICS AND COMPOSITES
Task 12122

Ceramic materials are used where special properties, such as chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and mechanical and chemical resistance to temperature extremes, are required. Ceramics, such as glasses, refractory concretes, geothermal cements, porcelains, and high-density ceramics, are used in many commercial applications: e.g., substrates for electronic packaging, containers for nuclear waste disposal, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, thread guides and wear surfaces for the manufacture of paper and clothing, cutting tools and cutoff wheels for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for the coal-conversion and petrochemical industries. In defense applications, these materials are used as radomes, missile nose cones, turbine components in portable electric-generating facilities, and bearing surfaces in gyroscopes. Because they are brittle, structural ceramics are usually over-designed to satisfy engineering requirements or are not used, even though they have other outstanding properties. The investigation of the fracture and deformation properties of these materials may overcome many of the difficulties associated with their brittle behavior and permit ceramics to be used more effectively.

Composite materials are highly engineered, heterogeneous materials designed to impart unique, superior properties not achievable with conventional materials. Composites offer the possibility of high-strength, lightweight, durable structures. In typical advanced composites, the strength-to-weight ratio is an order of magnitude larger than normal grades of steel. Extensive commercialization of composites will result in major energy and materials savings, increased productivity, improved product safety, and improved U.S. technological innovative capabilities. For effective industrial utilization of composites materials, better understanding of their wear-out and multiple-crack fracture mechanisms is needed. Test methodologies and standards must be developed, the effect of flaws and interface debonding must be assessed, and damage accumulation must be accurately inspected and evaluated.

Our program on ceramics and composites has as its objectives: (1) generation of new theory and data to elucidate fracture and deformation mechanisms in nonmetallic materials, (2) development of new techniques for studying the fracture and deformation properties of materials, (3) collection of engineering data for structural applications, (4) investigation of degradation processes that result in erosive and abrasive wear of nonmetallic materials, and (5) investigation of the microstructure of nonmetallic materials and their relationship to mechanical behavior. Experimental techniques developed by the Division permit measurements of the mechanical properties of composites and ceramics over a wide range of conditions: in vacuum at temperatures to 2973 K, in corrosive environments at temperatures that range from room temperature to 1873 K, and in cryogenic environments at temperatures as low as 4 K. This range of experimental capabilities is unique.

Fundamentals of Fracture
Subtask 1 of Task 12122

S. W. Freiman, T. A. Michalske, E. R. Fuller, Jr., S. M. Wiederhorn

In this subtask, studies are being conducted to elucidate basic fracture and deformation mechanisms in ceramic materials. Because water plays such a dominant role in the fracture of ceramics, our main effort during the past year has been directed at elucidation of mechanisms of subcritical crack growth in glass. Glass was selected as a material for study both because of its practical value as an engineering material and because it serves as a model for brittle ceramics that are subject to subcritical crack growth. Work during the past year has resulted in four significant findings that relate to basic fracture mechanisms in glass. These are: (1) an elucidation of the factors that influence the stress sensitivity of the stress corrosion rate, (2) a determination of the chemical route for subcritical crack growth in glass, (3) a clarification of the factors that determine the stress corrosion limit in glass, and (4) a characterization of the role of ion exchange in the fracture of binary silicate glasses.

Electrostrictive Processes During Fracture. At normal temperatures and pressures, water is known to have a strong influence on the fracture behavior of ceramics and glasses. Acting as a stress-corrosion agent, water causes crack growth in ceramics and glasses when these materials are subjected to an applied stress. An ideal way of studying the crack-growth process is through the use of fracture mechanics techniques, which permit the crack-growth rate to be quantified in terms of the applied-stress-intensity factor. Experimental investigations using these techniques have shown that the crack velocity can be expressed as an exponential function of the applied-stress-intensity factor. Expressed in this manner, crack-growth data can be explained in terms of reaction rate theory. The fact that the position of the crack-growth curves depends on the temperature and chemical potential of the water in the test environment is consistent with reaction-rate theory. During the past year, a theory was developed in which it was shown that the slope of the crack-growth curves can also be explained in terms of reaction-rate theory. In particular, it was shown that the slope of the crack-growth curve depends on electrostrictive processes that occur at crack tips during bond rupture. If electrostrictive processes are important during fracture, it follows that the slope of the crack-growth curve will be affected by the stress dependence of the dielectric constant of the glass or ceramic and by the dielectric constant of the fluid in the vicinity of the crack tip. During the past year, we have shown that both of these predictions are reasonably supported by experimental data. However, further experimentation is needed to fully substantiate the theory. The critical experimentation required to evaluate this theory will be conducted during the coming year.

Chemical Reaction Path. Although it has been recognized for many years that water is the principal agent for subcritical crack growth in glass, the reaction path for the crack-growth process has not been well understood. Work performed on vitreous silica during the past year has shown that a key factor in the reaction process is the ability of water molecules to act both as electron acceptors and electron donors. The experimental evidence for this conclusion is based on crack-growth studies conducted on silica glass in a

variety of chemical environments. Environments such as ammonia, hydrozine, and formamide, which also have the ability to accept and donate electrons, were also shown to support subcritical crack growth in silica glass. Environments that did not possess this chemical property behaved as inert environments with regard to crack propagation. Environments in the latter category include nitrobenzene (which has a large dipole moment) and carbon monoxide (which can donate, but not accept electrons). As a result of this work, a detailed molecular model for the reaction of siloxane bonds (Si-O) with water (or other active environments) has been developed. Implications of the model with regard to the stress corrosion susceptibility of other brittle materials are currently being pursued. Because of its potential scientific and technological implications, this work has been submitted to Nature for publication.

Crack-Tip Blunting in Glass. The theoretical model of stress-corrosion cracking proposed by Charles and Hillig for glasses and ceramics is based on the assumption that the stress-corrosion process can be described by reaction-rate theory. The rate of chemical reaction depends on the stresses at the crack surface and increases as the stresses increase. Near the crack tip the reaction rate is high because the stresses are high. A consequence of this theory is the prediction of a stress-corrosion limit: a stress below which cracks become blunt and crack growth is severely retarded. During the past year, direct confirmation of this prediction of the Charles-Hillig theory was obtained by using fracture mechanics techniques to study subcritical crack growth in soda-lime-silica glass. By loading double-cantilever-beam-type specimens at a stress intensity factor that was less than the fatigue limit, crack blunting was demonstrated, as evidenced by microscopic tear marks on the fracture surface and by a hysteresis in the crack-growth behavior. These results support the concept that fracture in glass occurs by a chemical route that is similar in nature to that occurring during the corrosion of glass. The results of this study were presented at the International Symposium on the Fracture Mechanics of Ceramics, July 15-17, 1981, at Pennsylvania State University and will be published as part of the proceedings of that conference.

Stress Corrosion of Binary Glasses. During the past year a study was conducted to determine the effect of alkali-ion migration on the fracture properties of binary alkali-silica glasses. Crack-growth data were collected on soda-silica glasses using one molar solutions of cesium and lithium nitrate. For the range of crack velocities studied (10^{-9} to 10^{-5} m/s), crack velocity curves obtained using lithium-nitrate solutions as test media always lay at a higher value of K_I and had a steeper slope than curves obtained using cesium-nitrate solutions. These results suggest that the rate of ion exchange between the glass and the solution at the crack tip played an important role in controlling the crack-growth rate. Using infrared spectroscopy to study the corrosion of the binary glasses in these solutions, a correlation was made between the crack-growth data and the corrosion process. A heretofore undiscovered plateau in the crack-growth curve, observed at very low velocities, was linked to the silica dissolution rate in these glasses. In the coming year, these studies will be continued to further elucidate the importance of corrosion to the crack-growth process.

New Approaches to Fracture and Deformation
Subtask 2 of Task 12122

E. R. Fuller, Jr., S. W. Freiman, S. M. Wiederhorn, R. J. Fields, N. J. Tighe, E. D. Case

The techniques of fracture mechanics provide engineers with new methods for estimating the total allowable lifetime under load when mechanisms of failure are well understood. For ceramic materials, the primary mechanism of failure at low temperatures is subcritical crack growth, whereas that occurring at elevated temperatures is creep and creep cracking. Crack nucleation and flaw generation may also be important to the failure process at elevated temperature. For ease of design, it is useful to have a single diagram, or set of diagrams that represent the complex behavior of ceramics at elevated temperatures, especially when several mechanisms are active in influencing strength or fracture behavior. The fracture maps and deformation maps developed originally by Ashby are an example of this type of diagram. These diagrams define fracture or deformation behavior in terms of temperature and applied stress. During the past year two new kinds of maps have been developed by the Fracture and Deformation Division to describe the effect of temperature and time on the strength and fracture resistance of ceramic materials.

Crack-Growth Maps. Crack-growth mechanism maps were developed to define the crack-growth behavior of metals or ceramics at elevated temperatures. The maps are applicable to subcritical crack growth, which can account for a significant fraction of component lifetime in high temperature applications. The independent parameters on this type of map are the applied stress intensity factor and the temperature; the dependent parameter is the crack velocity. The map is used to display crack-growth data and to categorize the various mechanisms of subcritical crack growth at elevated temperatures. This sort of map emphasizes changes in a material's fracture mechanisms as either a K or temperature change and thereby displays various regions of a material's crack-growth response (in terms of these variables). Data have been obtained for silicon nitride, a nickel-based superalloy, and an aluminum alloy. Mechanisms have been proposed to explain various regions of behavior on these maps. The results of this work were presented at the Fifth International Conference on Fracture held in Cannes, France, 29 March to 3 April, 1981, and have been published as part of the proceedings of that conference. The work on this project is supported jointly by Tasks 12121 and 12122.

Strength-Degradation Maps. The second type of map developed as part of Subtask 2 relates to the strength of ceramic materials at elevated temperatures. Recent experiments on structural ceramics at elevated temperatures suggest that time-dependent processes such as creep, crack growth, cavitation, and pit formation, have an important influence on the long-term structural reliability of these materials. Since these processes are stochastic, fracture-mechanics-based theories of structural reliability are not as useful at elevated temperatures as they are at low temperatures. Strength-degradation mapping provides an alternative to the pure fracture mechanics approach for lifetime prediction. Although the approach is more probabilistic in nature and suggests the use of probability density functions to describe the time evolution of strength, concepts of fracture mechanics can be factored into the approach. Probabilistic concepts of strength are used for the construction of strength-degradation maps,

which relate strength failure time and failure probability on a single diagram. These maps provide a general picture of the failure behavior of a ceramic material and can be used to establish engineering loads and temperatures that are consistent with engineering behavior. A map of this sort has already been constructed for hot-pressed silicon nitride (NC 132), which is currently being used in experimental heat engines. Two papers on this subject will be published as part of the International Symposium on Fracture Mechanics of Ceramics, held at Pennsylvania State University, July 15-17, 1981.

Engineering Evaluation of Ceramics
Subtask 3 of Task 12122

E. R. Fuller, Jr., N. J. Tighe, S. M. Wiederhorn, S. W. Freiman, R. S. Polvani, D. E. Roberts, C. L. McDaniel, R. F. Krause, Jr.

Extensive studies are being conducted on the strength of ceramic materials that are intended for use in a number of important commercial and defense applications. Materials being studied include: geothermal cements that will be used to line the wells that tap hot reservoirs of water deep within the earth, specialty ceramics that are intended for use in heat engines, dense ceramic materials for prosthetic devices, dielectric materials for ceramic capacitors intended for defense applications, and refractories for regenerative heat exchangers used in MHD applications.

Geothermal Cements. The program on geothermal cements was initiated to develop a laboratory test facility for screening candidate cementing materials that are to be used in finishing operations of geothermal well holes. The program provides the technical data necessary for an evaluation of the structural integrity of these cements after they have been exposed to high pressure, high temperature brine. The suitability of these cements for more costly tests in down-hole facilities will be evaluated for the Department of Energy (DOE). The program is divided into several tasks aimed at establishing the mechanical and physical properties of cements after they have been exposed to simulated geothermal environments. Properties include flexural and compressive strengths, strengths of cement pipe interfaces, and cement permeability at high pressures and temperatures.

During the past year, work at NBS has been spent equally on laboratory-exposed cement compositions and on compositions exposed in the Cerro Prieto Mexican geothermal field. Laboratory tests were conducted on selected cements that were exposed either to water at 473 K and 20 MPa pressure or to a 20 percent salt solution at 573 K and 20 MPa pressure for periods of one to four weeks. Following the exposure of the specimens, their compressive strength, tensile strength, shear-bond strength (to steel), and water permeability were measured at room temerature. Strengths were found to range from $\sim$ 10 MPa to 100 MPa, depending on the cement composition, and little difference was observed between tests conducted in brine and those tested in water.

Tests on the durability of 16 cement compositions in the Cerro Prieto geothermal field were done in cooperation with the Mexican Comision Federal Electricidad and the Instituto de Investigaciones Electricas (IIE). Test specimens to go into the well were prepared at NBS and IIE. After exposure, the test specimens were shared by IIE and NBS researchers to compare methods of determining

compressive strength and water permeability. Although exposures were initiated in April of 1981, specimens are not yet available for testing since exposure times of 3, 6, and 12 months are required for the program. Research on geothermal cements is expected to continue through the coming year.

High Temperature Structural Ceramics. Because ceramic materials offer the potential for significant increases in operating temperature and efficiency for gas turbine engines, silicon nitride and silicon carbide are being considered by the Department of Defense (DOD) and DOE for application in heat engines. The Division is contributing to these programs by evaluating the applicability of proof testing as a method of ensuring the structural reliability of heat-engine components, and by studying the mechanisms by which these materials fail at elevated temperatures.

The objectives of the program on proof testing are three-fold: (1) investigate long-term effects of high temperature on the strength of silicon carbide and silicon nitride, (2) determine the physical and chemical conditions that limit the applicability of proof-testing as a method of improving the reliability of these ceramics, and (3) characterize the conditions of environment and temperature that result in strength-impairing flaw generation in silicon nitride and silicon carbide. It is expected that this program will provide a base of experimental data upon which a modified theory of component reliability can be built.

During the past year, studies on this program have resulted in the development of a new method of analysis of high temperature strength degradation of structural materials (the strength-degradation maps discussed in the preceding section). Experimental data required for the construction of strength-degradation maps were collected in this part of our research program. Over two hundred specimens of hot-pressed, silicon nitride (NC 132) were tested for periods ranging from 0.5 h to 1000 h at a temperature of 473 K and an applied load of 250 MPa. Transmission electron microscopy was used to identify the various mechanisms of strength degradation or strength enhancement that resulted from this exposure. Four kinds of behavior were identified: crack growth, crack healing, pit formation, and creep cavitation. Data from this year's work will appear as part of the Proceedings of International Symposium on Fracture Mechanics of Ceramics held at Pennsylvania State University, July 15-17, 1981. Work on this subject will be continued during the coming year with the objective of developing strength-degradation maps for other structural ceramics [Al_2O_3, $MgO \cdot Al_2O_3$, and hot-pressed, silicon nitride (NCX34)].

The second part of the Division's program on structural ceramics is concerned with evaluating mechanisms of fracture at elevated temperatures. The specific objectives are to characterize high temperature deformation and crack growth and fracture behavior of structural ceramics that have potential application in coal conversion systems. To measure crack velocity as a function of stress-intensity factor, an analysis of the four-point bend test was made that allowed the crack length, stress-intensity factor, and the crack velocity to be calculated from the points on a load-deflection curve. Hence, a notched, four-point bend test can be used to yield information on both fracture toughness and crack velocity as a function of stress intensity for a broad range of stress-intensity factors. The results of this research were also presented at the International Symposium on Fracture Mechanics of Ceramics. Data are currently

being collected on a variety of experimental compositions of Sialon type materials (manufactured for NBS by Dr. K. Kobayashi of the National Industrial Research Institute of Hyushu, Japan). The four-point bend technique is being used as a method of relating the chemistry and microstructure of these materials to their mechanical behavior.

Finally, to develop a basic understanding of high temperature mechanical behavior, a grain-boundary-creep crack-growth-model was developed to explain subcritical crack growth in ceramic materials at elevated temperatures. The model is based on the assumptions that (1) the crack propagates along grain boundaries by a coupled process of surface and grain boundary self-diffusion, (2) the adjoining grains on either side of the boundary behave elastically, and (3) steady-state conditions prevail. The model predicts the following relation between crack velocity, v, and stress intensity factor, K:

$$K/K_{mm} = \frac{1}{2}\left[(v/v_{min})^{1/12} + (v/v_{min})^{-1/12}\right]$$

where $K_{mm} = 1.69\ K_G$ and K_G represents the stress intensity below which crack growth does not occur. In terms of the conventional expression, $v \alpha K^n$, the present model predicts the value of n ranging from a minimum of 12 to infinity, depending on the value of K. The value of 12 is consistent with values reported for Sialons and for hot-pressed silicon nitride. Results of this work have been accepted for publication in the Journal of the American Ceramic Society.

Bioceramic Materials. Another new and interesting application of ceramic materials is in the field of medicine. Certain types of ceramic materals (aluminum oxide, glass ceramics) are useful as structural components of prosthetic devices because they are biologically inert to the body environment and are relatively strong compared with bone. Consequently, these materials are being introduced into the body in several applications: total hip replacements, anchors for artificial teeth, and artificial knee joints. Given the tendency for ceramic materials to undergo stress-corrosion cracking due to water in the environment, there is concern over the ability of these materials to perform their function in the body environment for extended periods. Because of this concern, the Division has been conducting a study to determine the effect of microstructure on stress-corrosion cracking of aluminum oxide.

During the past year stress rupture and stressing rate tests were conducted to evaluate crack-growth parameters needed for the prediction of the lifetime of ceramic prostheses. Data were collected on biological quality aluminum oxide in water using three-point flexure as a test procedure. To simulate effects at body temperature, all tests were conducted at 310 K. Stressing rate tests were conducted at three stressing rates covering three orders of magnitude in time to failure. Stress rupture tests were conducted using the pneumatic loading fixtures described in the last annual report. Failure times were monitored on all statically loaded specimens for a period of two weeks. The intent of the study was to compare these two techniques for gathering crack-growth information. Several techniques were used to analyze the data; the technique that seems most promising is the trivarient linear regression procedure, which yields the Weibull modulus, m, as well as the slope, n, of the K-v data. Results to date indicate reasonable agreement between the results

of tests conducted by the two techniques; however, scatter in the data was substantial so that firm conclusions on lifetime under load could not be made from these data. In the coming year we hope to obtain more accurate measurements on the biological grade aluminum oxide by using the controlled-flaw technique which will provide a well-defined fracture origin for failure. By the end of the coming year, we should have accurate data for lifetime predictions on this material.

Screening Tests for Ceramic Capacitors. The objective is the development of screening tests to assess the performance and expected lifetime of ceramic capacitors. Studies include the use of ultrasonic signals combined with sophisticated computer-analysis techniques as a means of detecting delaminations and cracks in capacitors, characterization of the microstructure of the ceramic capacitors, and measurement of the susceptibility of the ceramic material in the capacitor to strength degradation resulting from internal stresses and subcritical crack growth.

The importance of this project rests on the use of these capacitors in critical military applications that require high functional reliability; therefore, the mechanical and electrical reliability should be ensured to the highest technically achievable levels. Recent experience indicates that the chance of capacitor malfunction in military hardware is sufficiently high as to cause real concern to the Department of Defense. Symptoms of malfunction (dielectric breakdown of the capacitor) often occur after the capacitors have been installed in components, which results in expensive repair operations that add significantly to the cost of military hardware. Furthermore, since malfunctions often occur some time after installation, the reliability of operating systems may suffer as a result of capacitor malfunction. To alleviate these problems, research is being conducted to develop a better understanding of the causes of failure and to develop techniques to screen out defective capacitors.

During the past year, crack-growth data on two grades of capacitor materials were obtained using the stressing rate technique. The data suggested a substantial difference in behavior of these two materials: the crack-growth behavior of one of the materials was similar to that of glass, whereas the other behaved more like a high grade aluminum oxide. The data were used to measure the allowable residual stresses in the assembled ceramic chip capacitors: a minimum strength of $\sim$ 15 MPa (2 ksi) was predicted for the capacitor material that behaved in a way similar to glass, whereas, the minimum strength for the other capacitor material was approximately 25 MPa (3.5 ksi). These strengths were somewhat lower than the maximum stress (determined by the Draper Laboratory), $\sim$ 5 ksi, which occurs during the mounting of these capacitors to electronic substrates. The low value of the minimum strength probably accounts for the fact that these capacitors fail primarily from corners in service, where the stresses are highest. Results of this work were presented under the title, "Allowable Residual Stress for Ceramic Chip Capacitors," at the 83rd Annual Meeting of the American Ceramic Society held in Washington, D.C., May 3-6, 1981. Work on this subject will be continued during the coming year in collaboration with the Draper Laboratory.

Refractories for MHD Applications. Refractory materials are used for MHD air preheaters. The high temperature plasma (2673 to 2973 K) necessary for operable and economically attractive open-cycle MHD power generation is achievable

through the combustion of fossil fuels using air preheated to about 1773 K. Such temperatures require the operation of regenerative heaters at temperatures as high as 1923 K; the heaters require refractory materials that are capable of maintaining their mechanical integrity at this extreme temperature. Creep resistance is one of the primary properties that will determine the ability of refractories to perform adequately as components in regenerative heaters. Although several types of commercial refractory bricks have been selected to serve in this application, creep data on these materials are not available at temperatures exceeding 1773 K. The objective is to obtain the necessary data on the high temperature compressive creep of the refractories being considered for use in MHD air preheaters and to rank the proposed refractories in terms of their creep resistance at the service temperature of 1673 to 1923 K.

A high temperature test facility was built to provide the capability for obtaining data on twelve samples. Each station consists of a frame with a furnace that has provisions for testing three specimens simultaneously. The load for each specimen is applied with a pneumatic cylinder with the capacity to apply a 1.3 kN (300 lb f) load. The applied load is measured with a load cell and the specimen deflection is measured with a LVDT. The test facility has four furnaces and thus has the capability for conducting twelve experiments. The facility was designed to use a microprocessor to program and control the furnace temperatures and to interface with desired alarm signals. With this system, temperature cycles can be established easily and used to simulate actual service temperature cycles. The loads are applied to the specimens using rams made from SiC or Al_2O_3 as required by the specimen reactivity and test temperature. Fixtures for four-point bend flexure tests also have been constructed of SiC and of Al_2O_3 so that both types of specimen can be tested as required.

Dimensional stability data were obtained for the three materials used in the experimental air heat exchanger at Montana State University: (1) sintered chrome-magnesia (55 percent MgO, 20 percent Cr_2O_3, 11 percent FeO, 8 percent Al_2O_3), (2) fused cast magnesia spinel (65 percent MgO, 35 percent Al_2O_3), (3) fused cast α-alumina in a β-alumina matrix.

The yield stress, dimensional stability, phase structure, and compressive creep at 0.3 to 1.4 MPa (50 to 200 psi) were obtained for these materials for exposures of 168 h at 1673, 1773, and 1873 K. It was apparent from the results on these three materials that materials selection criteria based solely on reaction to slag in a nonstress condition could not predict the catastrophic effects of fracture and slag penetration that occurred as a result of creep fracture.

The chrome-magnesia samples exhibited poor creep resistance and swelling due to phase changes. Both processes caused extensive stress cracking in the test specimens. In slagging conditions, these cracks filled with slag and continued exposure led to erosion of the upper brick material, excessive penetration of slag, clogging of air passages, and premature failure in the air preheater test facility.

The fused cast $\alpha + \beta$ alumina, although it had better creep resistance, fractured during cooling under load. Such fracture is commonly observed in α-alumina, which is known to be subject to thermal shock twinning particularly in the temperature range 873 to 1073 K. The potential catastrophic effect of such fractures was demonstrated when the air preheater containing this material was disassembled. Extensive cracking occurred throughout the core, but mostly in the cooler bottom region. The core was held together by the coal slag that filled the cracks. In our temperature cycling experiments, the creep in one week under ΔT of 373 to 473 K produced creep equivalent to that observed in 1000 h at constant temperature.

The fused-cast, magnesia spinel exhibited good creep resistance even in samples saturated with coal slag. This material was very porous and the strain from creep was accommodated easily by microcracking. The catastrophic failure observed in the other materials did not occur in this material.

Based on the accomplishments during the first two years of our program, it is clear that the acquisition of static fatigue or creep data under constant and cyclic temperature conditions provides important information on behavior of refractories for high temperature, structural applications. The reduced-cross-section creep specimen we devised has provided valid, reproducible engineering data on a variety of refractory materials. During the program we have developed a microstructural analysis capability that can be exploited to provide mechanistic information on high temperature deformation of refractories. With the completion of the twelve-specimen, high temperature test facility we can more easily obtain data over long time intervals.

Friction and Wear of Ceramics
Subtask 4 of Task 12122

S. M. Wiederhorn, B. J. Hockey, E. R. Fuller, Jr., D. E. Roberts, R. S. Polvani

Friction and wear are important phenomena that determine the cost and reliability of precision-ground ceramic parts. Since machining often accounts for 90 percent of the cost of these parts, a considerable reduction in cost may be achieved by improving the machining process. Furthermore, since machining and erosion leave residual damage that reduces the strength of ceramic components, an understanding of these processes may lead to improvement in their strength. To achieve these ends, this project has been initiated to study the friction, wear, and erosion resistance of commercially important ceramic materials.

During the past year, work on the erosive wear of ceramic materials was directed toward (1) the analysis of an extensive set of erosion data on a wide variety of ceramic materials, and (2) the construction of a dynamic hardness apparatus capable of measuring hardness in times of as small as $\sim$ 1 ms. In addition, a new program was initiated to investigate static friction that occurs as the result of high temperature contact between ceramic components.

Erosion Measurements. During the past few years, erosion data were obtained on a variety of ceramic materials (soda-lime-silica glass, silica glass, silicon, silicon nitride, aluminum oxide, sapphire, and silicon carbide) as a function of temperature and particle velocity. Silicon carbide particles, 150 μm diameter, were used to erode the surfaces. The erosion-rate data

suggest that the erosion depended strongly on the critical stress intensity factor of the target material and on the particle velocity; by contrast, the erosion rate did not depend strongly on the temperature of exposure. These data were compared with two theories that have been proposed to explain the dependence of the erosion rate on the target properties (fracture toughness and hardness) and the particle properties (velocity, size, and density). To obtain an unbiased comparison between theory and experiment, a dimensional analysis was conducted on the five parameters given above, and an equation containing three dimensionless groups was obtained that could be used to describe the erosion process. A least-squares analysis of the experimental data was then used to evaluate undetermined exponents of the dimensionless equation. A comparison of the empirically determined constants with those expected theoretically suggests that both theories provide a qualitative explanation of the dependence of erosion rate on particle velocity and target properties. The most significant difference between the experimental data and the theoretical equations was the dependence of wear rate on hardness and toughness of the target; the dependence on these material properties was greater than predicted theoretically. This difference in behavior was attributed to the effect of microstructure on erosion and the statistical nature of the impact process. This work is currently being prepared for publication.

Dynamic Hardness Measurements. Because of the importance of hardness to the nucleation of cracks during erosion, an attempt is being made to measure the dynamic hardness of ceramic materials. Two approaches were taken to obtain estimates of the dynamic hardness. The first was directed at the characterization of acoustic signals generated during impact, so that an impact-load, time profile could be obtained for real-time impact situations. The impact apparatus has been constructed, is currently operational, and is being used for investigations of dynamic hardness of metals and ceramics under Tasks 12121 and 12122. Experiments conducted on aluminum plates during the past year are discussed under Task 12121 of this report. Future investigations will also be conducted on plates of soda-lime-silica glass.

The second method of measuring the dynamic hardness is based on the use of an electrically driven hardness indenter to apply loads to specimens for durations of ~ 1 ms. An experimental apparatus has been constructed for this purpose. The equipment has the capability of holding a constant load for a period of ~ 2 ms, the load being measured by piezoelectric load cell. The equipment, as constructed, is capable of delivering a maximum load of ~ 50 g, which is satisfactory for initial studies of the hardness of ceramic materials. A higher load capability is needed, however, to explore fully the effect of dynamic impact on the hardness and fracture of brittle materials. To achieve the higher load, a current-controlled amplifier will be purchased in the coming year. Experiments will then be conducted on a variety of ceramic and metallic materials to investigate the effect of time of loading on hardness.

Effect of Contact Damage on Strength. This new area of work for the Division is intended to enhance our understanding of contact damage in structural ceramics. The work will be divided into three parts: (1) a study of junction formation and adhesion resulting from high temperature exposure, (2) an investigation of the effect of junctions on the shear and tensile strength of contact surfaces, and (3) an investigation of mechanical and chemical means of altering the rate of formation of junction to reduce adhesion.

During the past year, a major portion of our time has been spent on the construction of experimental equipment to study frictional effects that result from adhesion. Two sets of equipment were constructed: one to study the friction of flat plates, at temperatures as high as 1273 K; the second to study the friction of spherical contact surfaces at temperatures as high as 1673 K. The first piece of equipment has been constructed and tested on glass microscope at temperatures as high as 373 K. The second set of equipment is nearing completion.

Studies to date on glass indicate a pronounced effect of temperature on the coefficient of friction. As the temperature is increased, the friction coefficient of soda-lime-silica glass is found to increase precipitously at about 573 K from a value of $\sim$ 0.5 to $\sim$ 1.3. The increase occurs at a temperature of $\sim$ 473 K below the annealing temperature of this glass. A similar effect of temperature on friction was observed previously by Rabinowicz and Imai on oxide forming ceramics. Studies conducted on a high-lead glass gave results that were similar to those obtained on soda-lime-silica glass. By contrast, silica glass showed no such enhancement of the friction coefficient over the same temperature range (room temperature to 873 K). Studies on this subject will be continued during the coming year.

Microstructure of Ceramics
Subtask 5 of Task 12122

B. J. Hockey, N. J. Tighe

The objective is to investigate the relation between structural and mechanical properties of ceramic materials. Techniques of high resolution TEM and SEM are developed and applied to study deformation, fracture, and wear processes in hard materials.

During the past year, work was directed toward (1) evaluation of our new microscope, (2) analysis of dislocation networks associated with crack tip interfaces, and (3) effects of temperature and stress on the microstructure of hot-pressed silicon nitride.

Crack-Tip Interfaces: Analysis of dislocation networks found at numerous crack interfaces in impacted and indented Al_2O_3 has been completed. These TEM results provide definitive proof that the dislocations are interfacial misfit dislocations associated with spontaneous crack closure and are not slip dislocation structures due to in-plane shear deformation. Qualitatively similar observations have also been obtained for SiC, Si, and Ge. The results, therefore, demonstrate the reversibility of fracture and, accordingly, the chemically active nature of fracture surfaces in brittle materials. As such, they provide further support for the concept of atomically sharp cracks.

Preliminary results have also been obtained on TEM studies aimed at investigating the role of plastic deformation at crack tips in more ductile materials. Specifically, dislocation emission has been observed at cracks in MgO and twinning has been found at the tips of cracks in $BaTiO_3$ after room temperature microfracture. In MgO, deformation appears to be associated with changes in crack direction and orientation, whereas in $BaTiO_3$ twinning appears to be associated with crack arrest.

Analytical Microscope. Most of the effort in this area has been devoted to evaluating and demonstrating the high resolution analytical and imaging capabilities of the new Philips 400 STEM unit. In particular, lattice imaging techniques have been successfully applied to a number of materials including hot-pressed Si_3N_4 and Al_2O_3, $BaTiO_3$, $Pb(Zr,Ti)O_3$, Si, and Au, and a resolution of 0.2 nm (lattice:Au) has been demonstrated. In addition, preliminary results bearing on the general microstructure, defect structure, grain-boundary structure, and included phases in several commercial grade barium titanates and lead-zirconia titanates have been obtained.

There is presently a lack of information on the microstructural changes associated with deformation in polycrystalline structural ceramics. With installation of the scanning transmission electron microscopy, we have the capability for carrying out microstructural analyses with sufficiently high resolution to identify inclusions, phases between grain boundaries, and defects at grain boundaries and interfaces. These analyses are done using energy dispersive x-ray, electron diffraction, and diffraction contrast and structure imaging.

Such analysis of silicon nitride samples that were deformed during static fatigue tests identified the failure mechanisms operative at different stress levels and for different time periods. For example, examination of the tension and compression sides of bent specimens showed that cavitation and crack formation associated with creep occurred in specimens subjected to a 250 MPa nominal bending stress for one week and six weeks. Similar specimens exposed without stress showed cavitation related to diffusional processes of oxidation but not the same crack formation. Examination of the tension side showed that some grain deformation occurred and suggested grain rotation and movement under creep conditions.

This type of analysis has just started and will be continued during the next fiscal year.

Engineering Evaluation of Composites
Subtask 6 of Task 12122

M. R. Kasen, R. E. Schrammn, R. D. Kriz, H. M. Ledbetter, C. F. Fortunko

Reliability of components fabricated from filamentary-reinforced composite materials is intimately related to an understanding of the failure modes of such materials. Widely differing properties of the reinforcement and matrix plus the high degree of anisotropy results in initial "failure" by damage accumulation on a global scale rather than by initiation and propagation of a unique crack as is the case for metals. The problem is exacerbated by lack of understanding of what constitutes "failure" in an engineering sense and by a lack of understanding of the factors contributing to performance variability in these complex materials. The problem must therefore be approached from a combined engineering and scientific point of view to define properly the nature of the problems and to lay the framework for a systematic fundamental approach to solutions.

Variability in composite material performance stems from intrinsic factors such as flaw content or cure state of the matrix resin and also from extrinsic factors reflecting the widely differing products sold under generic designations. During the past year, work has continued in cooperation with industry to establish standard grades of composite laminate for use in critical applications such as magnetic fusion energy technology. The work is based on the prior development of standard cryogenic grades of glass-reinforced epoxy industrial laminates designated G-10CR and G-11CR. Both the inherent material variability and the variability between products produced by differing industrial firms to the same specification have been evaluated. This information has been used to refine the specifications to minimize variability while simultaneously providing maximum manufacturing flexibility.

Industrial experience and research activities have defined the need for several variants of the cryogenic-grade laminates. Two such variants of G-10CR, one incorporating a lightweight fabric reinforcement for thin sections and one incorporating a polyimide resin matrix for improved radiation resistance, have been screened for their 4 K mechanical performance.

The use of composite laminates as thermal standoffs transitioning between 295 K and 4 K in cryogenic systems creates the need for accurate thermal conductivity characterization over this temperature range. Very low conductivities make accurate measurements difficult, and in the past, there has been significant differences in the results obtained by different laboratories on the same material. Cooperative work between NBS and CERN suggests that the differences are instrumental. It is anticipated that this problem will be solved in the near future.

Elastic properties, such as Young's modulus and the related property and internal friction, are fundamental to characterizing and understanding filamentary-reinforced composite materials. Several theoretical and experimental studies are in progress: (1) relationships between microscopic (constituent) properties and macroscopic (composite) properties in a cooperative program with the University of Colorado using theories based on scattered plane waves that predict sound velocities and elastic constants; these theories will be extended to ultrasonic attenuation, having been tested successfully for boron-aluminum and graphite-epoxy, (2) detection of mechanically induced damage; experiments show that the Young's modulus in graphite-epoxy can either decrease or increase depending on the deformation mechanism while internal friction always changes oppositely, (3) relationship between static and dynamic elastic constants using theory and experiment to clarify this frequently confusing correspondence, (4) internal friction of interfaces, just beginning, will probe the interrelationship among three sources of internal friction--filler, matrix, and interface, and (5) stress-induced interface strains in crossply laminae where misaligned anisotropic connected layers have strongly anisotropic interfacial strains that have been calculated from the full set of elastic constants.

Factors controlling the integrity of the interface between adhesively bonded thick sections of nonmetallic composite laminate and thick metal sections are of importance in large superconducting magnet technology. A program has begun to develop an ultrasonic nondestructive evaluation method of assessing damage accumulation of such interfaces as the result of mechanical or thermal stress. A low frequency, bulk-wave ultrasonic inspection system was developed

that permits inspection of the adhesive interface through the laminate. By operating at lower frequency, the scattering loss, caused by scattering from the fiber reinforcement, is substantially reduced. Therefore, inspections of relatively thick composite sections can be carried out.

Angle-ply laminates fabricated from fiber-reinforced materials have demonstrated significant damage accumulation prior to fracture in the form of ply cracks and interply delaminations. The effect of extreme environmental conditions (cryogenic temperatures, moisture) on the internal residual stress state and subsequent damage accumulation was investigated to understand better how the accumulated damage can influence the final fracture strength. Preliminary experimental tests show a substantial difference in the pattern of accumulated damage prior to fracture when exposed to varying environmental conditions. Analytic models have provided the necessary insight into understanding the fundamentals to the damage process prior to fracture by using a rational mechanistic approach (fracture mechanics).

A fundamental investigation on how an idealized plane wave propagates through unidirectional fiber-reinforced materials has resulted in a new technique to monitor significant changes in stiffness due to extreme environmental conditions. Increased use of high strength, lightweight, fiber-reinforced materials has resulted in exposing these materials to extremes in humidity, temperature, and radiation. Stress waves propagating through a graphite fiber-reinforced polymeric material were shown to be significantly shifted in direction as a result of absorbed moisture, reducing the material elastic stiffnesses. Radiation damage and large temperature changes are other obvious candidates. Excellent correlation between theory and experiment has verified that a shift in the direction of propagation of stress waves can be used to calibrate significant changes in the elastic response of a fiber-reinforced material when exposed to extreme environments.

An extensive review of the effect of cryogenic temperatures on the mechanical and thermal performance of composite materials was published during the year, updating similar publications in 1979. This review illustrated that the primary deficiency in state-of-the-art nonmetallic composites is embrittling of the resin matrix on cooling, decreasing the critical defect size, and contributing to increased property variability. Individuals at the Ciba Geigy Polymer Research Laboratory in Basel, Switzerland, have discussed various approaches to this problem with NBS staff members and have indicated an interest in a cooperative program to achieve solutions.

ELASTIC-PLASTIC FRACTURE MECHANICS
Task 12123

Safety and durability are primary considerations in the design and construction of engineering structures. Sophisticated methods to assess structural safety and durability have been developed on the basis of linear-elastic fracture mechanics. These analytical methods are applicable to the high-strength alloys used for aerospace vehicles and to the heavy-section steels used for nuclear pressure vessels. Unfortunately, the methods of linear-elastic fracture mechanics do not apply to a wide range of metal structures, including bridges, pressure vessels, ships, offshore structures, and pipelines, because in these applications, the materials of construction (steels and aluminum alloys are typical) are highly plastic (nonlinear) before fracture. Consequently, the assessments of structural safety and durability are based on empirical methods and prior experience. Although current methods usually provide a reasonable record of structural safety, improved efficiency and productivity could be achieved if more rational methods were used to establish material-toughness requirements, allowable stress levels, minimum service temperatures, and weld-quality standards. The objective of this task is to establish the scientific basis (i.e., elastic-plastic fracture mechanics) for developing fracture-prevention procedures applicable to materials that exhibit extensive plasticity before fracture.

Fracture Mechanics Relationships

H. I. McHenry, D. T. Read, R. B. King, Y. W. Cheng

The application of elastic-plastic fracture mechanics to the assessment of structural safety hinges on the development of analytical relationships among applied strain, required toughness, and flaw size. The approach used to establish such a relationship for the elastic-plastic case is to measure the driving force for fracture as a function of strain in tensile panels with a given flaw size and configuration. The driving force for fracture is measured in terms of the J-contour integral (J) or the crack tip opening displacement (CTOD). If one assumes that fracture occurs when a critical value of J or CTOD is reached, then the measured driving force is the same as the required toughness. Thus, each test results in an empirical relationship among applied strain, flaw size, and required toughness that is directly applicable to the specific specimen configuration. Tests are being conducted on a variety of specimen flaw configurations to provide a data base to evaluate critically the theoretical models and finite element analysis methods of relating applied strain, required toughness, and flaw size.

Procedures for the direct measurement of J are based on the definition of the J-integral as given by Rice:

$$J = \int_\Gamma W\, dy - \vec{T}\cdot\partial\vec{u}/\partial x\, ds \qquad (1)$$

where W is the strain energy density, $\vec{T}$ is the traction vector, $\vec{u}$ is the displacement vector, x and y are Cartesian position coordinates, and s is arc length along the contour, Γ. A convenient contour for evaluating J follows free surfaces along the y direction and traverses the tensile axis at a location remote from the crack. Measurement of the J-integral along this contour requires determination of the strain energy density along the y-direction contour segments and measurement of traction and displacement vectors along the x-direction segments. The strain-energy density is obtained using strains measured along the contour and the stress-strain curve of an uncracked tensile panel. The y-components of the traction and displacement vectors along the x-direction contour segments are measured using strain gauges and LVDTs, respectively. The change in displacement with position, du/dx, is calculated from the measured displacements. During a typical test, approximately one hundred J-vs-ε data points are obtained. Each point is computed from about twenty-five measured values of strain, displacement, and load.

The J-contour integral has been measured as a function of strain, ε, for HY 130 steel plates using several specimen configurations. The results for a series of single edge notch tensile specimens with notch lengths of 1, 2, 4, 7, and 20 mm indicate that the functional form of the dependence of J on strain is usually parabolic, then linear. The parabolic region at low strains is the region of linear-elastic fracture mechanics. The slopes of the linear parts of the J-vs-ε curves depend on crack length. As the crack length decreases to low values, deformation changes from net section yielding to gross section yielding, and the slope of the J-vs-ε plot decreases sharply.

Finite element analyses have been conducted to calculate J vs ε for comparison with the experimental results on HY 130 plates. Analyses that assumed plane stress overestimated the measured values of crack mouth opening displacement (CMOD) and J; yet excellent agreement was observed with the experimental load-displacement and limit-load results. The introduction of a small, stiffened zone that provides partial through-thickness constraint around the crack tip considerably reduced the disagreement. The stiffening effect was incorporated in the two-dimensional elastic-plastic analysis by use of an overlay technique in which two elements of the same shape and connectivity replace each single element near the tip. One of the elements is modeled as plane stress material and the other, plane strain. Simple adjustment of the specified element thickness provides the desired value of the stiffening parameter.

The experimental and analytical results clearly indicate the importance of crack tip region constraint (CTRC), which significantly reduces the applied J values at strains above yield for crack lengths less than the specimen thickness. Understanding of this transition is essential for the assessment of small defects, such as weld defects and surface cracks. The plane stress--plane strain overlay technique offers promise as a means of accounting for CTRC without resorting to three-dimensional nonlinear computations.

The demonstrated usefulness of the J-integral as a measure of the driving force for fracture and as a fracture criterion for two-dimensional configurations makes it desirable to apply J in a similar fashion to three-dimensional configurations such as surface flaws. Recent research at NBS has demonstrated that the J-integral for line contours about part-through cracks is path independent for two special planes. These planes are the planes of symmetry for part-through

cracks and include the plane of maximum depth of a semielliptical surface flaw. Thus, the point of maximum J along the front of a surface flaw can be evaluated using the line J-contour integral.

Given that J is path independent for the plane of symmetry of a surface flaw, it is possible to measure J vs ε using the procedures described previously. For a surface flaw centered with respect to width and length in a tensile panel, the measurement contour is in the center-width plane and extends from the crack plane up the front face of the specimen, through the thickness, and down the back face of the specimen to the crack plane. A series of surface-flawed tensile panels of API 5LX-70 pipeline steel were instrumented and tested to measure J and crack opening displacement (COD) vs ε.

The experimental results of J (and COD) vs ε were compared with analytical results obtained using the line-spring model. In this model, the surface flaw is treated as equivalent to a through-thickness flaw of the same length that is subject to closure forces and moments due to the presence of the uncracked ligament. The closure forces are computed by balancing the forces and moments such that the COD of the through-thickness crack is compatible with the COD of an edge-cracked panel with the same thickness and crack depth as the surface-flawed panel. The ligament is treated as an elastic, perfectly plastic spring, and thus, the magnitude of the closure forces and moments remains constant after ligament yielding. The elastic, perfectly plastic spring and the constant-depth crack assumptions result in considerable simplification of the analysis, thereby avoiding the necessity of computerized numerical methods. The excellent agreement between the experimental and analytical results for both COD and J suggests that the simplifying assumptions are reasonable and that a useful and convenient method for surface-flaw calculations is available.

Fracture Toughness

H. I. McHenry, I. H. Lin, J. G. Early, Jr.

In elastic-plastic fracture mechanics, fracture toughness is generally measured in terms of J or CTOD. As currently measured, fracture toughness is not a geometry-independent material property for steels in the transition region between linear-elastic and fully ductile fracture. The critical values of J or CTOD depend on the three-dimensional stress-strain behavior in the vicinity of the crack tip, i.e., on the CTRC. Available information indicates that CTRC is a function of geometry, type of loading, and strain hardening. Thus, a predictive fracture criterion for the elastic-plastic case should be proportional to a material property, such as the plane strain fracture toughness, K_{Ic}, and should be scaled by a function of CTRC.

A study of fracture-characterizing parameters was initiated at NBS by Dr. M. G. Dawes of the Welding Institute, Abington, England. Dr. Dawes performed the research at the Boulder Laboratories during a six-month visit starting in July 1980. The experimental program addresses the influence of CTRC on observed fracture behavior. Especially large errors can be introduced by present measurements of critical J-integral or CTOD values for the onset of cleavage fracture; large measurement variations are due to differences in CTRC between laboratory test specimens and cracks in structures. For example, the critical

values of J or CTOD obtained in deeply notched single edge-notched bend (SENB) specimens may grossly underestimate the toughness associated with identical material at the tips of smaller SENB specimens or at shallow surface cracks in large structures. Although published research indicates a growing awareness of these situations, there appears to be no generally acceptable method available at this time to determine the magnitude of the CTRC. The approach being taken is to obtain a comprehensive set of elastic-plastic fracture data (both J and CTOD) on a C-Mn steel for specimen designs having a wide range of plastic constraint. These data will demonstrate geometry dependence and establish an empirical basis for developing a parameter to characterize the influence of plastic constraint.

A theoretical study of cleavage fracture is being conducted to complement the empirical studies. A model is being developed that is an extension of the work of Ritchie, Rice, and Knott. It uses the strain-field solutions of Hutchinson to predict stress-state effects on the brittle-to-ductile fracture-mode transition. The experimental data will be used to evaluate the resulting theoretical predictions. In addition to plastic constraint effects, metallurgical factors are being investigated, particularly grain-size effects.

Significance of Defects

H. I. McHenry, C. M. Fortunko, M. B. Kasen, R. E. Schramm, Y. W. Cheng

A program is being conducted to establish weld-quality requirements for the Alaska Natural Gas Transportation System (ANGTS). Analytical studies involve modeling of the significance of defects using methods comparable to those used for the trans-Alaska pipeline assessment conducted previously. Experimental studies involve the measurement of CMOD as a function of remote strain for tensile panels with surface flaws. The results of these experimental and analytical studies will be used to assess the validity of the critical COD models used in the trans-Alaska oil pipeline. These models have been reassessed and their sensitivities to applied stress and material tensile flow properties compared and evaluated.

The extent to which the through-wall dimension of typical weld flaws, such as porosity and slag, is limited by the depth of a weld pass is being studied in pipeline girth welds. Confirmation of such an inherent limitation would greatly simplify the application of fracture mechanics principles to welds inspected by conventional radiography. Both multiaxis radiography and serial sectioning are used in this work.

The probability of fracture initiating from blunt pipeline girth weld flaws is being assessed in a program that subjects weldments containing slag, porosity, and arc strikes to low-cycle, strain-controlled, fully reversed fatigue within the plastic range. Results to date indicate that such flaws have a very low probability of initiating failure in weld metal of the toughness used in pipeline construction. The results are supportive of the concept that the allowable content of such flaws is more properly established on the basis of the percentage obscuration of a radiographic film than on flaw dimensioning. A program is being conducted to develop a series of reference radiographs suitable for implementation in this approach.

Ultrasonic inspection methods are being developed for determining the depth of flaws in weldments. Initial objectives relate to the fitness-for-service standards being developed for the ANGTS system. Emphasis has been on the development of electromagnetic acoustic transducers (EMATs) to size defects. The EMATs excite horizontal shear (SH) waves in the weldments that are reflected by flaws in proportion to their depth. A prototype EMAT system has been designed, built, calibrated, and evaluated for inspecting pipeline girth welds. The results to date indicate that the EMATs have a sufficient signal-to-noise ratio to effectively size flaws in pipeline girth welds. The emphasis of future research will be on developing the physical basis through parametric studies to permit industry to build a system for field applications.

Ultrasonic inspection techniques, using SH waves, are also being developed for austenitic stainless steel weldments. It has been shown that SH wave probing signals are particularly suitable for nondestructive evaluation (NDE) of stainless steel welds that exhibit transverse-isotropic texture. In such welds the propagation characteristics of SH waves are less complicated than vertically polarized shear (SV) and longitudinal (L) waves. In particular, it is possible to transmit SH waves through the weld metal-base metal interface without generating additional ultrasonic signals by mode conversion and reflection effects. The experimental work is being carried out in parallel with a theoretical investigation that is conducted by Dr. C. M. Fortunko (NBS, Boulder) and Prof. S. K. Datta (University of Colorado, Boulder). It is hoped that this research will lead to improved ultrasonic NDE techniques for stainless steel weldments that will provide defect size information for fracture mechanics assessments.

Low-Temperature Properties

R. P. Reed, R. L. Tobler, H. I. McHenry, J. M. Arvidson, T. A. Whipple

A major developing technology is the use of superconducting magnets in energy applications. High magnetic fields are required for fusion-plasma and MHD-plasma confinement and guidance. Superconducting machinery, under prototype development, provides the potential for better performance coupled with lighter weight and reduced space requirements. Power transmission via superconducting underground cables is under intensive development. Energy storage, using large superconducting rings, is being considered. In all applications, the magnet or superconductor, with appropriate structural supports, is expected to operate at liquid-helium temperature (4 K) up to twenty years.

Such emphasis on liquid-helium design and material use has led to large national materials programs sponsored by DARPA and DOE and managed by our Division. These programs have produced a low-temperature materials handbook; mechanical, thermal, electrical, and magnetic characterization of economical structural alloys including austenitic stainless steels, aluminum alloys, and superalloys; an annual Low-Temperature Materials Workshop held each October in Vail, Colorado; and joint research programs with subcontractors, which have included Battelle, Westinghouse, General Electric, Martin-Marietta, Teledyne-McKay, Alcoa, Armco, ESCO, and Belfour-Stulen. Major research emphasis has been to characterize the austenitic stainless steels (AISI 304, 316, and 310 grades), to develop reliable welding processes and filler metals for welding

steels, and to develop stronger, tougher austenitic stainless steels for use at low temperatures. The development and characterization of low temperature composite insulator standards is discussed in the previous task.

We are developing and characterizing a new class of austenitic stainless steels. Interstitial strengthening of a conventional austenitic Fe-Cr-Ni alloy is achieved by adding nitrogen, and increased alloy formability and nitrogen solubility limits are achieved by adding manganese. We are studying the influence of nitrogen and manganese on the temperature dependence of the flow strength, activation energies and volume, martensitic transformations, fracture toughness, and fatigue-crack-growth rates from room temperature to 4 K. Results indicate that the dependence of flow strength on nitrogen concentration increases dramatically at low temperatures. Nitrogen additions suppress both the body-centered-cubic and close-packed-hexagonal martensitic transformations. A linear relationship between fracture toughness (from J-integral measurements) and tensile yield strength at 4 K has been identified. The temperature dependence of the flow strength is critically dependent on austenite stability; low austenite stability results in strain-induced martensite formation, which produces low flow strengths. The anomalous stress-strain behavior resulting from these phase transformations has been analyzed and reported.

The role of low ferrite and small grain size in improving low temperature weldment fracture toughness has been and is being studied.

The U.S./USSR scientific exchange program on Cryogenic Materials and Welds is being maintained by the National Science Foundation. The temperature-dependence of the flow strength in Fe-Cr-Ni alloys at low temperatures is being studied jointly by NBS and the Physico-Technical Institute of Low Temperatures, Kharkov, USSR. The USSR group reports three ranges of anomalous behavior attributed to dislocation tunneling, phase transformations, and magnetic transitions (Neél). Our data do not confirm these findings, and the study is continuing to resolve the disparities.

Elastic Deformation Phenomena

H. M. Ledbetter

Our effort on solid-state elastic constants comprises three categories: (1) measurements; (2) analysis, correlations, theory; (3) theory-observation.

Our measurement studies deal with metals and alloys, composites (both fiber and particle reinforced), resins, and polymers. Many of these materials we study versus temperature down to four kelvins. Ongoing studies include: (1) beryllium, (2) NbTi/Cu superconductive wire, (3) titanium alloys, (4) Mn-alloyed stainless steels, (5) carbon- and nitrogen-alloyed stainless steels, (6) stainless-steel welds (including some containing delta ferrite), (7) delta-ferrite castings, (8) particle-reinforced aluminum, (9) glass-fiber-epoxy, (10) graphite-epoxy, (11) polymethyl methacrylate, (12) epoxy resins, (13) several polymers.

Analytical-correlational-theoretical studies in progress include: (1) error propagation during elastic-constant matrix inversion, for both cubic symmetry and hexagonal symmetry; (2) calculations of Debye characteristic temperatures from single-crystal elastic constants; (3) graphical representations of various elastic-constant surfaces; (4) prediction of single-crystal elastic constants for stainless steels from polycrystal elastic constants; (5) prediction of upper and lower elastic-constant bounds of textured aggregates and application to stainless-steel welds.

In-progress theory-observation studies include: (1) in collaboration with S. K. Datta, a scattered-plane-wave theory for predicting macroscopic elastic constants of fiber-reinforced composites, including the anisotropic-fiber case, and application to boron-aluminum and graphite-epoxy; (2) in collaboration with S. K. Datta, a theory for predicting elastic constants of a ring-layered composite and application to NbTi/Cu superconductive wire; (3) just beginning, theories are being developed for predicting properties of particle-reinforced composites.

Other current elastic-constant studies are described briefly in the section of this report on composite materials.

Test Methods and Standards

C. G. Interrante, R. deWit, J. G. Early, S. R. Low, J. H. Smith, G. E. Hicho

The development of test methods and standards for characterizing and specifying materials is a major activity of the Fracture and Deformation Division. The need for specific test methods and materials standards is often initially identified through our failure-avoidance efforts conducted for other Government agencies. The current activities are summarized as follows:

Development of Standard Reference Materials (SRM). Under the sponsorship of the NBS Office of Standard Reference Materials, SRMs have been prepared for calibrating instruments used to determine the percentage of retained austenite in ferrous alloys. The SRMs were prepared using metal powders of austenite and ferrite phase materials. The powders were blended, compacted, and sintered using powder metallurgical procedures. The samples were then calibrated using x-ray fluorescence and quantitative metallographic techniques and certified for sale. During the past year 167 fifteen-percent, 200 five-percent, and 200 thirty-percent austenite in ferrite SRMs were offered for sale by the Office of Standard Reference Materials. In the coming year, an SRM containing 2.5 percent austenite in ferrite will be prepared. The availability of this series of SRMs is essential for the accurate calibration of x-ray diffraction equipment used for determining the retained austenite in ferrous materials purchased accordingly to specifications that place a maximum on the amount of retained austenite allowed.

Standard Test Methods for Hydrogen-Assisted Cracking. Hydrogen-assisted cracking (HAC) is a significant cause of unexpected fracture in structures made from ferrous alloys. Reliable test methods for assessing the susceptibility to HAC are required to reduce the costs associated with these failures through control plans that use crack-growth-rate data and threshold fracture-toughness data. A method for real-time measurements of crack-length and crack-growth

rates, and hence stress-intensity and threshold fracture toughness, in double-cantilever-beam (DCB) test specimens has been developed at the NBS. This test method has broad applicability for studies of the fracture behavior of metals and alloys in environments that promote slow crack growth.

In earlier work on the measurement of the thermal diffusivity of hydrogen in metals, an original test method was developed at the NBS using palladium specimens. This test method has applicability to the diffusivity of hydrogen in ferrous alloys, and it can be used for assessing the potency for hydrogen charging associated with various hydrogen/metal systems.

A project has been initiated to use neutron-inelastic scattering to determine the effect of local stress fields on the local atomic interaction between hydrogen and iron atoms in specimens of steel under stress. Modifications to the NBS reactor time-of-flight spectrometer have been completed. Tests carried out on nonferrous alloys by Reactor Radiation Division staff indicate that hydrogen detection in the 1 to 100 ppm range is feasible.

Development of Test Methods for Assuring the Safety of Pressure Vessels. Research is continuing on programs for the Office of Hazardous Materials Regulations (OHMR) to develop appropriate test methods and provide the basis for developing standards for the safe shipment of hazardous materils in portable pressure vessels. Work has been completed on assessing the validity of various mechanical properties tests used for acceptance of homogeneous seamless steel cylinders. The results of this program will permit a fair and equitable comparison to be made between cylinders manufactured in the U.S. and in foreign countries and to ensure the same level of safety for all classes of cylinders. A program has been initiated to assess the fracture toughness of various cylinders and to assess the need for requiring fracture toughness requirements on materials for use in seamless steel vessels.

An extensive program was initiated this year to develop reliable test methods and acceptance standards for the use of composite pressure vessels for the transportation of hazardous materials. At present, attention is focused on cylinders made by overwrapping aluminum cylinders with fiberglass-reinforced plastic and Kevlar. Tests are being assessed and developed for assessing the safety of these vessels in ambient environments, high temperature environments, and in aqueous environments. The results of these tests will be used by OHMR to develop specifications for allowing wide-scale use of composite cylinders.

Analysis of Shipbuilding Materials Standards. The initial effort in a Coast Guard sponsored program to evaluate a group of 60 U.S. and foreign shipbuilding materials specifications has been completed. The results of these detailed comparisons have identified technical areas of commonality, difference, and omission that could have a major impact on component performance. The Coast Guard will use the conclusions developed by this study to reduce the current case-by-case determination of equivalence and its inherent possibility of inconsistent determinations of acceptability. The Society of Naval Architects and Marine Engineers has scheduled an oral presentation of this work in addition to journal publication. Future emphasis will be placed on developing a written manual for the Coast Guard outlining the specific technical criteria that must be considered in such material comparisons to assist Coast Guard personnel in making new evaluations of materials acceptability.

Development of Standards for Resource Recovery. With the recent adoption by ASTM of the first two national voluntary consensus standards for municipal ferrous scrap developed by Committee E28 on Resource Recovery, Subcommittee E38.02 on Ferrous Metals, with NBS staff in a leadership role, has now focused its efforts on developing an adequate data base for establishing precision and accuracy limits for specification E701, "Standard Methods of Test for Municipal Ferrous Scrap." A round robin test program with six participating laboratories has been created to develop this data base. With the cooperation of an agency of the Ontario, Canada, government through use of their facilities, almost one hundred synthetic samples of ferrous scrap are being prepared for the round robin tests.

Terminology. Our work in the area of terminology is concerned mainly with terminology for fracture testing and it includes staff participation in an international committee, ISO TC164/WG on Terminology for Mechanical Testing, as well as in several national committees, the ASTM Committee on Terminology, ASTM Subcommittee E-24.05 on Terminology for Fracture Testing, and the ASM Committee on Definitions of Metallurgical Terms. The Chairman and Secretary of SC E-24.05 serve in a diversified set of roles to facilitate and coordinate the development of terminology within the many task groups of eight subcommittees of Committee E-24. This terminology includes development definitions, descriptions of terms, recommended symbols, abbreviations, and units, as well as guidelines for use of the SI Metric Practice. Another aspect of this work is the coordination of the terminology of E-24 with that of other ASTM committees and other national and international bodies concerned with terminology for fracture testing.

ASTM Task Group E-24.06.02--Application of Fracture Analysis Methods. Membership in this task group involves participation in a predictive round robin whose objective is to verify experimentally whether or not analytical methods currently in use can predict failure of complex structural components containing cracks from results of laboratory tests. The results of a great deal of analytical work done over a year ago are still being coordinated by the Task Group.

ASTM Task Group E-10.02-C on Interpretation of Charpy Data. Membership in this task group involves participation in the development of a standard for Computer Analysis of Charpy Impact Test Data, and it has included the writing of an NBS Appendix for this proposed standard. The appendix is titled, "General Method for Computer Analysis of Charpy Impact Data." In 1981, Committee E10 decided to abandon this effort because several negative votes cast in a committee-level ballot were upheld. If time permits, the NBS will write a state-of-the-art paper on this topic, and in this paper the negative votes can be addressed.

Other Activities of the Fracture and Deformation Division

Invited Talks

Fracture Modes of G-10CR in Compression
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
B. A. Beck
October 1980

Microcracking in Single Phase Ceramics Due to Thermal Expansion Anisotropy
Materials Science and Engineering Seminar, Pennsylvania State University, University Park, Pennsylvania
E. D. Case
October 1980

Aluminum Weldments
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
J. W. Elmer
October 1980

Ultrasonic Detection and Sizing of Weld Defects
1st Conference on Fitness-for-Service in Shipbuilding, Boulder, Colorado
C. M. Fortunko
October 1980

Atmospheric Mechanisms of Fracture Resistance
International Symposium on Fracture Mechanics of Ceramics
Pennsylvania State University, University Park, Pennsylvania
E. R. Fuller, Jr.
October 1980

Hydrothermal Effects on Microstructure and Strength of Refractory Concretes
ASM Materials and Processes Congress, Cleveland, Ohio
E. R. Fuller, Jr.
October 1980

Erosion of Brittle Materials
Materials and Processes Show and Congress, Cleveland, Ohio
B. J. Hockey
October 1980

Notch-Bar Impact Testing
Mechanical Engineering Seminars, Department of Mechanical Engineering, University of Maryland, College Park, Maryland
C. G. Interrante
October 1980

Radiographic Evaluation of the Significance of Weld Defects
1st Conference on Fitness-for-Service in Shipbuilding, Boulder, Colorado
M. B. Kasen
October 1980

Elastic Constants of Fiber-Reinforced Boron Aluminum. A Critical Comparison of Observation and Theory
Metallurgy Department, Wayne State University, Detroit, Michigan
H. M. Ledbetter
October 1980

Code Approaches to Fracture Control
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
H. I. McHenry
October 1980

The Development of Fitness-for-Service Standards for Shipbuilding
1st Conference on Fitness-for-Service in Shipbuilding, Boulder, Colorado
H. I. McHenry
October 1980

NBS Program
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
R. P. Reed
October 1980

Low Temperature Material Properties
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
R. P. Reed
October 1980

Comparison of Corrosion and Stress Corrosion Rates in Alkali Silicate Glasses
Glass Division, American Ceramic Society, Bedford, Pennsylvania
S. W. Freiman
October 1980

Creep and Static Fatigue of Si_3N_4 at 1200 °C
American Ceramic Society, Fall Meeting, San Francisco, California
N. J. Tighe
October 1980

Cr-Ni-Mn-N Stainless Steels
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
R. L. Tobler
October 1980

Stainless Steel Weldments
NBS-DOE Workshop on Materials at Low Temperatures, Vail, Colorado
T. A. Whipple
October 1980

Ultrasonic Detection and Sizing of Planar Weld Flaws in the Long Wavelength Limit
1980 Ultrasonics Symposium, Boston, Massachusetts
C. M. Fortunko
November 1980

Significance of Three Dimensional Flaws in Pipeline Girth Welds
International Conference on Pipeline and Energy Plant Piping,
Calgary, Alberta, Canada
M. B. Kasen
November 1980

Effects on Moisture, Residual Thermal Curing Stresses and Mechanical
Load on the Damage Development in Quasi-Isotropic Laminates
ASTM Symposium on Damage in Composite Materials, Bal Harbour,
Florida
R. D. Kriz
November 1980

Fracture Behavior of 9-Ni Steel
GRI Conference in LNG Tank Safety, San Diego, California
H. I. McHenry
November 1980

Effects of Precracking Variables on Responses from Slow-Bend Charpy Tests
Presented by R. deWit (prepared by C. G. Interrante), CSNI Special-
ists Meeting on Instrumented Precracked Charpy Testing held at
EPRI, Palo Alto, California
R. deWit
December 1980

Status of Organic Insulators for Magnets
Conference on Electrical Insulators for Fusion Magnets, DOE,
Germantown, Maryland
M. B. Kasen
December 1980

The Organic Insulator Program at NBS
Conference on Electrical Insulators for Fusion Magnets, DOE,
Germantown, Maryland
M. B. Kasen
December 1980

Proposed Insulator Program at NBS
Conference on Electrical Insulators for Fusion Magnets, DOE,
Germantown, Maryland
M. B. Kasen
December 1980

Advantages of SH Waves for Nondestructive Evaluation of Stainless
Steel Weldments
EPRI, Palo Alto, California
C. M. Fortunko
January 1981

Advantages of SH Waves for Nondestructive Testing of Austenitic Welds
NDE Group, Lawrence Livermore Laboratory, Livermore, California
C. M. Fortunko
January 1981

Detection and Sizing of Flaws in Pipeline Girth Welds with Long Wavelength SH Waves
Golden Gate Metals and Welding Conference, San Francisco, California
C. M. Fortunko
January 1981

Wave Propagation and Elastic Constants in Particulate and Fibrous Composites
First Japan-U.S. Conference on Composite Materials, Tokyo, Japan
H. M. Ledbetter
January 1981

Where We Have Been and Where We Are Going in Our Quest for Dimensionally Stable Structural Materials for Gyroscopes
Semiannual Progress Report Meeting, Office of Naval Research, C. S. Draper Laboratory, Cambridge, Massachusetts
B. W. Christ
February 1981

TEM Study of Crack Tips
Special Symposium on Crack Tip Deformation at the 110th Annual Meeting of the AIME Society, Chicago, Illinois
B. J. Hockey
February 1981

Reliability of Assurance Aspects of Brittle Materials
Department of Mechanical Engineering, University of Ottawa, Ottawa, Ontario, Canada
S. M. Wiederhorn
February 1981

Energy Release Rates in Diffusive Crack Growth
General Electric Research and Development Center
T. J. Chuang
March 1981

Crack Growth Mechanism Maps
Fifth International Conference on Fracture (ICF5), Cannes, France
E. R. Fuller, Jr.
March-April 1981

Dynamic Effect of Liquids on Surface Crack Extension in Glass
Presented for T. A. Michalske, V. D. Frechette, and R. Hudson
Fifth International Conference on Fracture (ICF5), Cannes, France
E. R. Fuller, Jr.
March-April 1981

Slide Presentation on the Topic Union Tanks Re-Stress Relief Treatment
Presented to Staff Members of the Federal Railroad Administration, Washington, D.C.
S. R. Low
March 1981

Beryllium Microdeformation Mechanisms
Creep and Fracture of Engineering Materials and Structures
R. S. Polvani
March 1981

Temperature Dependence of the Yield Strength of Austenitic Cryostructural Alloys
E. O. Paton Institute of Electrowelding, Kiev, USSR
R. L. Tobler
March 1981

A COD Approach to Failure Criteria
Colloquia on Modern Topics in Mechanics, The Technological Institute, Northwestern University, Evanston, Illinois
R. deWit
April 1981

Ultrasonic Nondestructive Evaluation of Pipeline Girth Welds Using Electromagnetic-Acoustic Transducers
American Welding Society Annual Convention, Cleveland, Ohio
C. M. Fortunko
April 1981

Ultrasonic Nondestructive Evaluation of Pipeline Girth Welds Using Electromagnetic-Acoustic Transducers
Ames Laboratory, Iowa State University, Ames, Iowa
C. M. Fortunko
April 1981

MAPE MEHANIZAMA RAZVOJA PRSLINA (Maps of the Mechanisms of Crack Development)
Joint Seminar of Metallurgical Section of the Yugoslavian Chemical Society and Rheology Group of the Yugoslavian Society of Mechanics, Belgrade, Yugoslavia
E. R. Fuller, Jr.
April 1981

Atomistic Influences on Fracture Toughness
Institute of Physics, University of Zagreb, Zagreb, Yugoslavia
E. R. Fuller, Jr.
April 1981

Lecturer in course taught on Materials Toughness Measurement by Instrumented Impact Testing
American Society for Metals, Flow General Corporation, Tysons Corner, Virginia
C. G. Interrante
April 1981

Strain Dependence of J-Contour Integral in Tensile Panels
Fifth International Conference on Fracture (ICF5), Cannes, France
D. T. Read
April 1981

Strain Dependence of J-Contour Integral in Tensile Panels
Joint Meeting of Metallurgical Subgroup of Serbian Chemical Society and Yugoslav Society of Mechanics, Belgrade, Yugoslavia
D. T. Read
April 1981

Energy Release Rates in Diffusive Crack Growth
83rd Annual Meeting, American Ceramic Society, Washington, D.C.
T. J. Chuang
May 1981

Crack Growth in Polar Environments
83rd Annual Meeting, American Ceramic Society, Washington, D.C.
S. W. Freiman
May 1981

Effect of Region 2 on Stressing Rate Curves
83rd Annual Meeting, American Ceramic Society, Washington, D.C.
S. W. Freiman
May 1981

Stress-Intensity-Factor Dependence of Subcritical Crack Growth Rate
83rd Annual Meeting, American Ceramic Society, Washington, D.C.
E. R. Fuller, Jr.
May 1981

Strength of Refractory Concretes in High Temperature and Pressure Steam
83rd Annual Meeting, American Ceramic Society, Washington, D.C.
E. R. Fuller, Jr.
May 1981

Testing Geothermal-Well Cements
83rd Annual Meeting, American Ceramic Society, Washington, D.C.
R. F. Krause, Jr.
May 1981

Reliability of Ceramic Turbine Materials
New England Chapter, American Ceramic Society, Boston, Massachusetts
N. J. Tighe
May 1981

Allowable Residual Stress for Ceramic Chip Capacitors
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S. M. Wiederhorn
May 1981

Role of Error Propagation in Lifetime Prediction
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S. M. Wiederhorn
May 1981

Nondestructive Evaluation of Large Diameter Girth Welds Using Electromagnetic-Acoustic Transducers
Ultrasonics Applications Group, Rockwell International, Thousand Oaks, California
C. M. Fortunko
June 1981

Design of Analog Electronic Subsystems for Electromagnetic-Acoustic Transducers
Rockwell International, Thousand Oaks, California
C. M. Fortunko
June 1981

A Molecular Model for Stress Corrosion in Vitreous Silica
ONR-NBS Workshop on the Fracture of Brittle Materials, NBS, Gaithersburg, Maryland
S. W. Freiman
June 1981

Crack Propagation and Stress Corrosion of Glass
Gordon Conference on Glass, Plymouth, New Hampshire
S. W. Freiman
June 1981

Lattice Trapping-Influence of Discrete Crack-Tip Reactions on Crack Growth
ONR-NBS Workshop on Stress Corrosion Processes in Brittle Materials, NBS, Gaithersburg, Maryland
E. R. Fuller, Jr.
June 1981

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R. B. King
June 1981

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R. F. Krause
June 1981

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H. I. McHenry
June 1981

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H. I. McHenry
June 1981

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S. M. Wiederhorn
June 1981

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International Symposium on the Fracture Mechanics of Materials, Pennsylvania State University, University Park, Pennsylvania
E. D. Case
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Crack-Opening Displacement of Surface Cracks in Pipeline Steel Plates
14th National Symposium on Fracture Mechanics, UCLA, Los Angeles, California
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Effects of Composition on the Fracture Toughness and Slow Growth of SiAℓON
International Symposium on the Fracture Mechanics of Materials, Pennsylvania State University, University Park, Pennsylvania
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A Critical Evaluation of Fracture Mechanics Techniques for Brittle Materials
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S. W. Freiman
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August 1981

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October 1, 1980

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Metal Properties Council, Technical Advisory Panel
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Department of Energy, Office of Fusion Energy, Research Advisory Committee
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January 1981
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E. R. Fuller, Jr.

83rd Annual Meeting of the American Ceramic Society, Grain Boundary Structure and Characterization, Chairman
May 1981
B. J. Hockey

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May 1981
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The Technion, Haifa, Israel
October 15 - November 10, 1981
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POLYMER SCIENCE AND STANDARDS DIVISION

POLYMER SCIENCE AND STANDARDS DIVISION

Ronald K. Eby, Chief
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S. M. Thomas, Administrative Officer

In the seven decades since Leo H. Baekeland introduced the first commercial synthetic plastic produced entirely by the reaction of small molecules, polymers have left little of our economy, technology, industry, and culture untouched. We have moved rapidly into an age in which an overwhelming number of humanity's needs are served by polymers. The volume currently produced exceeds that of steel and forms the basis of industries which add over 90 billion dollars of value by manufacture (a measure of the relative economic importance of manufacturing among industries) and provide 3.4 million jobs. Recent summaries show that polymers research already accounts for about 47 percent of the total industrial R&D expenditure for metals, polymers, and inorganic materials. Among these materials, polymers also constitute about 39 percent of the value added by manufacture, 49 percent of the jobs, 45 percent of the number of scientific publications, and 39 percent of the ASTM standards.

Polymers have been shaped by intellectually sophisticated research which has been recognized by a number of Nobel Prizes. The resulting materials have contributed to national industrial productivity through their economy, ease of fabrication, and useful properties such as low density, corrosion resistance, and toughness. They are energy efficient; the largest volume polymer, polyethylene, uses 28 percent of the energy per unit volume required by steel for conversion from raw to refined material and yields further savings in processing and shipping. In fact, studies have shown that for every barrel of oil used to make plastic products, approximately one barrel is saved in comparison with the use of the next best alternative material. These useful properties have enabled polymers to contribute to increased productivity both by creating entirely new products and by substituting for other materials in existing products.

Polymers have entered increasingly sophisticated and demanding applications. Polyvinylidene fluoride films are used as electromagnetic transducers in high fidelity systems. Structural parts of aircraft are constructed from composites with a polymer matrix. Polyurethane elastomers are used to pump blood in circulatory assist devices. The list of such examples is very long, encompassing trends for the increased use of polymers in packaging, construction, transportation, national security, electronics, information handling, clothing, appliances, energy, dentistry, and medicine. Since polymer technology is on the steep part of the learning curve, these trends create many new needs for concepts, measurements, standards, and data that can be used to insure their reliable performance in the use, processing, and other phases of the material cycle.

To identify the key needs, the managers of the Polymer Science and Standards Division make structured visits with industrial and Government laboratories. Visits have included Bell Labs, DuPont, Johnson and Johnson, Army R&D Command, General Motors, Boeing, and Lawrence Livermore Laboratories. Surveys have been conducted in the areas of durability, composites, and processing. These and other contacts with research associates, experts in industry, trade associations, standards associations, guest workers, Government, and academia insure that the

Division's efforts are directed toward fostering the effective use of polymers in solving national problems. These national problems include the growth of industrial productivity, national security, efficient Government, materials utilization, conservation of critical materials, and reasonable regulation of the effects of technology.

The Division has used these activities as a basis for participating in budget initiatives to secure the resources necessary to meet emerging needs. For the budget cycles currently active, programmatic initiatives emphasize polymer matrix composites because of their role in increasing industrial productivity and substituting for critical materials. Specific areas encompass toughened hybrid matrix materials, high strength polymer fibers, methods of predicting durability, and methods of measuring and controlling matrix cure. Competence building initiatives on the science of forced Rayleigh scattering, polymer morphology, and time-resolved Fourier transform infrared spectroscopy have been prepared.

The present activities are associated into areas concerned with mechanical reliability in load-bearing applications, chemical durability and lifetime prediction including the migration of protective additives, characterization methods and standards for molecular composition and use properties, dielectric properties and electrical conduction, and reliable dental and medical materials. Substantial cooperative efforts are conducted with research associates from a number of industries, the Department of Defense, the National Institutes of Health, the American Dental Association, the Food and Drug Administration, and the Bureau of Engraving and Printing. All these efforts lead the scientists of the Division into productive examination of those properties of polymers which are of concern to people who use, design, and produce useful polymer objects. This work helps society capture, in safe and satisfying ways, the benefits of the increasingly widespread application of polymers.

In the following pages, the activities of the Division are presented formally in five tasks, each described separately:

12132	POLYMER STANDARDS FOR CONTROL AND EQUITY
12135	TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
12136	MECHANICAL DURABILITY OF POLYMERS FOR DESIGN AND USE
12138	MIGRATION AND THE DURABILITY OF POLYMERS IN USE
12139	DIELECTRIC AND PIEZOELECTRIC PLASTICS DESIGN AND PERFORMANCE

POLYMER STANDARDS FOR CONTROL AND EQUITY
Task 12132

This task provides molecular and gas transmission standard reference materials (SRM's) to a $30 B/year plastics and elastomers industry. Molecular SRM's are used extensively in industry to calibrate gel permeation chromatographs (GPC's) which are used routinely to measure polymer molecular weights and molecular weight distributions. The latter are the most important physical properties in determining a polymer's processability and its ultimate performance.

Improved characterization techniques are essential to providing improved SRM's. A fundamental knowledge of polymer solution properties such as osmotic pressure, viscosity, diffusional behavior, and scattering power is essential to this goal. As a consequence, a majority of the activities in this task involve experimental and theoretical studies of polymer solution properties. As a spinoff of our characterization activities, this task also provides data and concepts which are useful in polymer processing. Some of these activities during the past year include:

- Certification of a new, narrow-molecular weight polystyrene standard, SRM 1479 ($M_w \sim 10^6$).
- Continued development of a new state-of-the-art, self-calibrating gel permeation chromatograph.
- Approximately 300 gas permeation experiments which have been carried out for the purposes of upgrading the certificate for SRM 1470 to include He, CO_2, and N_2.
- Analytical and computer simulation studies of chain entanglements.
- Development and construction of a new state-of-the-art light scattering photometer. This instrument will have the option for static or dynamic light scattering measurements at elevated temperatures.
- Completion of a low shear rate rotational viscometer based on the floating rotor type (Zimm-Crothers). Viscosities may be determined at shear rates as low as 3.0 s^{-1} and up to 8.0 s^{-1} at temperatures up to 150 °C.
- Completion of a theory of the phase behavior of polymer blends.

Standards for Gas Transmission Measurements
Subtask 1 of Task 12132

J. D. Barnes

Gas transport properties of polymeric materials are vital in assessing end-use suitability and durability of polymers in such applications as packaging and coating materials. Facilities similar to the one developed at NBS should prove useful in quality control of processes for manufacturing film and sheet materials.

The NBS Automated Manometric Permeation Measuring Facility went into routine operation in February. Since that time, approximately 300 experiments have been performed. Each experiment represents a set of measurements at a given temperature and at a given upstream pressure, using one of four selected gases on three specimens. One hundred experiments are performed on each specimen of SRM 1470 for purposes of upgrading the SRM certificate to include He, CO_2, and N_2 in addition to O_2. The SRM certificate will also provide temperature and pressure coefficients for the time-lags and permeances. Figure 1 shows the pressure trace from a typical experiment. Note how, in the early phases of the experiment, sorbed gases from the previous experiment cause the pressure to rise in the cell even when no upstream pressure is applied. When this happens, the cells must be pumped out again. Upstream gas pressure is not applied until the pressure rise due to sorbed gases has fallen below an acceptable level. When the upstream pressure jumps from zero to the preset value (at the arrow in figure 1), there is no change in the trace until an induction period has passed. After a suitably long time, the pressure rises at a steady rate. The quantities characterizing the specimen are the induction period (time-lag) and the steady rate of pressure rise. Figures 2 and 3 give results for the rate of pressure rise and the time-lag of a typical specimen. The time-lag for He gas is less than one second and cannot be measured with our present setup.

The phenomenon of partial immobilization manifests itself when CO_2 is used as the permeant species in SRM 1470. The time-lag decreases by about 20 percent at any temperature as the upstream pressure increases from 45 kPa to 135 kPa. The shape of the time-lag pressure trace is also different in this case, but we do not yet have a solution to the transport equations which allow us to explicitly account for the contribution of partial immobilization when fitting data to the time-lag curve.

We found that data-taking totally occupied our apparatus and that it was necessary to send the data to the NBS central computer for reduction and analysis. In order to achieve this, we implemented a TIE into the NBS Net using software we developed ourselves. The data reduction programs have been copied into the 1108 and are presently being rewritten to take care of language and environment differences between the two machines. It is expected that all of the data for the new SRM 1470 certificate will have been analyzed by October 1.

During FY82, we expect to finish upgrading the data acquisition hardware in the automated manometric permeation measuring facility. This replacement of antiquated MIDAS data acquisition equipment by more modern equipment using the IEEE-488 bus will allow us to study films with shorter time-lags and higher transmission rates.

We expect to undertake experiments near the glass transition temperature of SRM 1470 in an effort to better understand the role of molecular motions in transport processes. It is also believed that the glass transition plays an important role in regulating partial immobilization.

We expect to begin development of a simpler measurement scheme based on gas chromatography that will allow us to study interactions between permeant species in multicomponent mixtures.

ASTM Activities
Subtask 2 of Task 12132

J. D. Barnes

J. D. Barnes continues to serve as chairman of ASTM Subcommittees F-2.30 (Test Methods) and F-2.93 (Statistical Matters) of ASTM Committee F-2 on Flexible Barrier Materials. Subcommittee F-2.30 is responsible for test methods relating to materials characterization, barrier properties, sealing and bonding properties, and additive migration. Subcommittee F-2.93 provides statistical assistance to all groups needing it within Committee F-2.

Dr. Barnes has drafted a Standard Practice for Selecting and Distributing Flexible Barrier Materials for Interlaboratory Testing Programs. This document is in the Subcommittee balloting stage, and it is expected that the adoption of this practice will enhance the ability of round-robin participants to obtain meaningful characterizations of the test methods they are studying.

Dr. Barnes is also a member of Subcommittees D-20.19 (Film and Sheeting), D-20.12 (Olefin Plastics), D-20.70 (Analytical Methods), and D-20.13 (Statistics) of ASTM Committee D-20 on Plastics. Dr. Barnes has played a very active role in reviving interest in Subcommittee D-20.13, and the group receives many more requests for statistical assistance than formerly.

Self-Calibrating Gel Permeation Chromatography
Subtask 3 of Task 12132

P. H. Verdier

Gel permeation chromatography (GPC) is a widely accepted technique for estimating the molecular weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide calibrants for each polymer measured of known molecular weight over the entire molecular-weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material, so that each new material requires a fresh calibration. The so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape and, in any event, is inadequate for quantitative determinations. Some instruments, an example of which is commercially available, attempt to circumvent the need for calibrants by adding a single-angle light scattering detector to the usual concentration-sensitive detector. However, this does not allow the extrapolation to zero scattering angle which is required, in principle, to relate scattering intensity to molecular weight. In addition, qualitative information on the variation of scattering with angle, normally required to give assurance that meaningful results are being obtained, is not available.

We are designing and constructing a light-scattering detector for the GPC which measures, in real time, the scattering intensity as a function of scattering angle and which is controlled by a dedicated minicomputer in a way that allows scattering to be measured as a function of scattering angle and concentration. The instrument will allow continuous monitoring of the variation of scattering with angle. This will allow immediate identification of difficulties such as

association, microgel formation, etc., which could affect the validity of the molecular weight obtained, an important consideration for work on new and unstudied materials. In addition to molecular weight, the mean-square radius (radius of gyration) will be obtained as a function of molecular weight, at least in the higher ranges of molecular weight, providing useful information for the characterization of branched polymers.

The mechanical components of the instrument have been constructed, and alignment is under way. The electronic components (preamplifiers, amplifiers, and switches) have been designed and prototypes built. In the coming year, we expect to complete alignment, construct the electronics, program the minicomputer and its associated video display, and begin taking measurements.

Dynamics of Polymer Chains
Subtask 4 of Task 12132

P. H. Verdier, D. E. Kranbuehl

The dynamic behavior of polymer chains is important to improving both characterization and processibility of polymers. The principal methods used to estimate molecular weight, and in particular gel permeation chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, non-equilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improvements in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

The processability and the final characteristics of both plastics and elastomers depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end-products. A major shortcoming of the present theory is its inability to treat chain entanglements in a realistic way. Our present work is aimed primarily at the study of entanglement effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems and serve to guide the development of better theoretical treatments.

Present work in this area is proceeding along three main lines. The first is a study of the effects upon our results of the necessarily crude models of polymer chains employed in our work. This study was prompted by the fact that our results show much larger effects of self-entanglement upon chain motion than are predicted by a currently popular theoretical model, which raises the question of the extent to which the effects we observe are artifacts of the models. We have extended our earlier studies of chain motion on several lattices to chains which are not constrained to lie on lattices. Perhaps surprisingly, the self-entanglement effects obtained for chains on lattices, which are largely independent of the lattice employed, become even more pronounced for chains free of lattice constraints. During the coming year, we expect to extend this work further by studying the motion of chains with move

rules modified to provide increased local randomness at each step and to write up the results for publication. Second, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasielastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. It appears that by direct simulation we may be able to resolve the disagreement, which will increase the value of measurements made by this relatively new technique. These studies have begun and should be completed in the coming year. Third, as a step in the direction of investigating melt properties, we have begun a study of systems of many interacting chains, with chain densities corresponding to concentrated solutions and melts. This work, which was partly supported this year by a grant from the NRCC, will be continued during the coming year.

Low Shear Rate-High Temperature Rotational Viscometer
Subtask 5 of Task 12132

H. L. Wagner, J. G. Dillon[1]

[1]FDA Guest Worker

Limiting viscosity number (intrinsic viscosity) is the most rapid and convenient method of measuring the molecular weight of high polymers provided the relationship between viscosity and molecular weight is known. However, for polymers greater than about a million in molecular weight, such as UHMWPE, the viscosity depends on shear rate as well as molecular weight. Hence, measurements should be made at zero or very low shear rate where this dependence is minimal and where, in addition, degradation due to shear is avoided.

A low shear rate rotational viscometer of the floating rotor type (Zimm-Crothers), which may be operated at the high temperatures required for polyethylene, has been designed and put into operation. Viscosities may be determined at shear rates as low as 3.0 s^{-1} and up to 8.0 s^{-1} at temperatures up to 150 °C. To assess the performance of the viscometer, measurements were made on several polystyrenes, two of which were Standard Reference Materials. The viscosity results were consistent with the previously published data on these samples, indicating that the instrument is operating satisfactorily.

Low shear rate limiting viscosity numbers for several samples of implant UHMWPE in decalin at 135 °C and a shear rate of 3.0 s^{-1} are shown in table 1, together with the results for these same polymers in capillary viscometers.

The multibulb capillary viscometer used here operates at shear rates of about 50 s^{-1} to 150 s^{-1}; the standard type of capillary viscometer ordinarily employed for routine viscosity measurements provides a shear rate of about 2000 s^{-1}. From the table it is seen that serious errors may occur if capillary viscometers are employed, even if extrapolation to zero shear rate is attempted using the multibulb viscometer.

A problem encountered in these measurements in the low shear viscometer is an initial rapid loss in viscosity of 2 to 3 percent during the first ten minutes of residence in the viscometer and as much as a 7 to 9 percent decrease in the

first hour. This does not occur with the polystyrenes available to us. Attempts are underway to understand and eliminate this difficulty.

Table 1

Sample No.	99716	99881	99974
Maximum Concentration	0.046%	0.03%	0.02%
Limiting Viscosity No.			
Decalin 135 °C			
(a) Zero shear rate (low shear viscometer, initial value)	17.7 dL/g	24.2 dL/g	37.8 dL/g
(b) Zero shear rate, estimated (multibulb viscometer)	18.9		34.0
(c) High shear rate (routine Canon-Ubbelohde viscometer)	14.6	17.8	26.0

Rubber and Rubber Compounding Standard Reference Materials
Subtask 6 of Task 12132

G. W. Bullman, G. B. McKenna

The process of streamlining the NBS Rubber SRM Program is continuing in response to reduced resources available for this program. As part of this reduction, rubber and rubber compounding Standard Reference Materials, for which NBS serves primarily as a warehouse facility, are being removed from the SRM list as inventories are exhausted. In addition, several materials are being removed from the list due to poor sales. These SRM deletions are being coordinated with ASTM Committee D-11 on Rubber and Rubber-Like Materials and Committee D-24 on Carbon Black to assure an orderly change in the ASTM standards and within the rubber industry.

In order to serve industry's needs for rubber SRM's with our reduced resource base, we are maintaining inventories of materials which industry (through ASTM) has indicated are important, even though NBS's primary function for these materials is to serve as a warehousing facility. For example, we recertified SRM 381 (N-tertiary-butyl-2-benzothiazole sulfenamide, a rubber accelerator) in order to maintain inventories of this material. In addition, proposals were written to OSRM requesting working capital funds for the procurement of materials and recertification of SRM's 371 (Sulfur) and 372 (Stearic Acid) during FY82.

Where standards involve certification of fundamental physical properties, we are issuing new SRM's when a need is indicated. Thus, during the past year we issued a new Butyl Rubber, Mooney Viscosity Standard (SRM 1495) with a lower Mooney Viscosity Number than that available with the Butyl Rubber SRM 388. This new standard extends the range of Mooney Viscosity Standards available to the rubber industry.

Static and Dynamic Configurational Properties of Polymer Chains: Theory
Subtask 7 of Task 12132

F. L. McCrackin, R. J. Rubin, C. C. Han, J. Mazur, I. C. Sanchez, D. J. Lohse[1]

[1]Exxon Chemical Company

Comprehension of the configurational statistics of polymer chains is indispensable for a rational characterization of polymer solution properties. Constitutive properties of a polymer which are dependent upon its configuration include the intrinsic viscosity, mean square dipole moment, the optical anisotropy, and the spectral dichroism. Mechanical properties are also intimately related to the configurational characteristics of the polymer chain.

The hydrodynamic radii of polymers were computed for polymer chains at the theta point created by a Monte Carlo simulation in which both volume exclusion and the energetics of nearest-neighbor interactions are taken into account. The dimensionless ratios ρ of the radius of gyration to the hydrodynamic radius were also computed. The calculated ratios of ρ were compared with experimental ratios measured by elastic and inelastic light scattering. The calculated ratios showed better agreement with the experiment ratios than did values calculated for the analytcal Gaussian coil model of the polymer. The Monte Carlo calculations are being continued for different coordination numbers of the lattice of the polymers and for nearest-neighbor interaction corresponding to good solvents. The results are being compared to the blob model of a polymer and to available experimental data.

A review paper has been completed and is presently in the hands of the Washington Editorial Review Board of NBS. It is intended that this review be published in the series, Advances in Chemical Physics, edited by I. Prigogine.

In this review, the theory of discrete step random walks in discrete time and continuous time is outlined. The relation between continuous time random walks and a generalized master equation is developed. In the limit of long walks, the following asymptotic properties are discussed: (1) return to the origin, (2) number of distinct sites visited, (3) central limit results, and (4) walks with steps of infinite variance. The effect of boundary conditions and traps on random walk behavior, maximum displacements and spans, and the application of Wald's identity for first passage time problems is treated in a chapter devoted to boundary conditions.

A general method is outlined for calculating the statistical properties of the number of visits to a set of points in a random walk. In illustrative examples, a number of known results and new results are easily derived: (a) the generating function of the probability distribution of a random walk of N steps with an excluded origin; (b) the generating function of the probability distribution of a random walk of N steps to go from point A to point B with no intermediate visits to A or B, i.e., a random walk with excluded origin and end point; and (c) the generating function of the probability of an N step random walk to visit a surface layer of points m times without ever crossing through the surface to the other side (i.e., penetrating the solution surface). This last result recovers a result obtained earlier by R. J. Rubin [J. Chem. Phys. 43, 2392 (1965)] for adsorption at a solution surface.

A statistical thermodynamic theory of a polymer solution is formulated which takes into account concentration inhomogeneities on size scales equal to or larger than the average size of a polymer chain. A generalized cell model is used as the basis for the new polymer solution theory. Closed-form, parametric equations are obtained for solvent and polymer chemical potentials which only reduce to classical (Flory-Huggins) potentials in concentrated solutions. The second virial coefficient A_2 varies as

$$A_2 \sim \frac{1}{Mc^*} \sim \begin{cases} M^{-1/5} & T \gg \theta \\ M^{-1/2} & T = \theta \end{cases}$$

where c^* is the overlap concentration (as defined in scaling theories) and M is the molecular weight. For finite M, A_2 vanishes slightly below θ. At $T = \theta$, the chains are still repulsive because of the existence of repulsive ternary monomer interactions. For the chain expansion factor α^2, we obtain

$$-c^* \, d\alpha^2/dc^\circ_{c=0} = \text{positive constant}; \; T > \theta.$$

This result implies that even in the dilute regime, chain dimensions should decrease with increasing concentration. The physics behind this result is that large fluctuations of the chain dimensions are damped because such fluctuations increase the probability of unfavorable interchain interactions. Neutron scattering experiments are being planned to check these predictions.

Polymer Blends
Subtask 8 of Task 12132

I. C. Sanchez, F. W. Wang, R. E. Lowry

Mixtures or blends of two or more different polymers can, under the proper conditions, produce materials with properties intermediate between those of the constituent polymers. This provides a method of tailoring a material to a specific application as well as optimizing the cost/performance ratio. Many plastic markets are primarily cost limited. Modern Plastics, a trade magazine says, "New polymer development is at a technological plateau. But new alloys--compounds of two or more structurally different polymers--are far more economical to develop than are generically new classes of plastics." Material costs are an important variable in the economic formula because the polymeric raw material is about two-thirds of the manufacturing cost of a typical plastic part.

A major generic problem associated with blends is the property that most polymer mixtures are incompatible and, given the opportunity, will phase separate. Although separated phases on a micro scale are often desirable, if the morphology and scale of the separated phases is not within acceptable limits, parts made from blends are useless. Since polymers tend to phase separate much more rapidly at the high temperatures encountered during processing, the phase separation problem is a matter of widespread concern which limits the rate of introduction of polymer blends.

Phase diagrams of liquid polymer/polymer mixtures (blends) are very unusual when compared to similar low molecular weight mixtures. Neither the familiar adage, "like dissolves like," nor the familiar observation that solubility increases with temperature are in general applicable to polymer blends. We have examined the thermodynamic and molecular reasons responsible for this unusual phase behavior. A general thermodynamic analysis of phase stability has been developed which suggests that thermally induced phase separation near a lower critical solution temperature is an entropy driven process. The entropic driving force is related to the compressible nature of a fluid mixture and the propensity of fluids to contract upon mixing (negative volume changes) at sufficiently high temperatures or, equivalently, sufficiently low fluid densities. By using a molecular equation of state theory, we have shown that volume contraction is always expected at low fluid densities if attractive interactions exist between dissimilar molecular species. All of the unusual aspects of polymer blend phase behavior can be given a rational basis.

There has been much effort to prepare polymer blends for the tailoring of polymers to specific end uses. A simple quantitative method for determining the point of polymer compatibility is needed. We have, therefore, initiated a project to develop a fluorescence energy transfer technique for the study of the phase behavior of polymer blends.

If the emission spectrum of a donor chromophore overlaps the absorption spectrum of an acceptor chromophore, nonradiative energy transfer can take place over distances as large as 5 nm. The theory of this process is due to Förster who obtained for the efficiency, Eff, of the energy transfer on the donor-acceptor separation, r, $Eff = [1+(r/R_0)^6]^{-1}$ where the sixth power of the characteristic distance R_0 is proportional to the overlap integral.

Intermolecular fluorescence energy transfer will take place in a film made of two almost identical polymers, one labeled with a small amount of a donor chromophore and the other labeled with a small amount of an acceptor chromophore. In a blend made of these chromophore-labeled polymers and a third polymer, the efficiency of intermolecular energy transfer will be larger when the third polymer is incompatible with the first two and form a separate phase than when it is compatible and serves as a diluting "solvent" for the first two. Thus, measurements of fluorescence energy transfer will allow us to determine the cloud point curve for the two practically identical labeled polymers and a third polymer.

We have synthesized donor- or acceptor-labeled polymers of narrow molecular weight distribution. We shall use the fluorescence energy transfer technique to determine the cloud point curve of these polymers and a third polymer.

Static and Dynamic Scattering from Polymers
Subtask 9 of Task 12132

C. C. Han, D. B. Minor, H. L. Wagner, A. Z. Akcasu[1], S. J. Bai[1], D. J. Lohse[2], T. P. Lodge

[1]University of Michigan
[2]Exxon Chemical Company

Scattering techniques, such as light and neutron scattering, provide valuable characterization information on polymers. Static light scattering from a dilute polymer solution is the classical method of determining the weight average molecular weight of a polymer. It is a method widely used in industry for this purpose. Static scattering measurements also provide two other important pieces of information: the equilibrium size of the polymer molecule, i.e., its radius of gyration, can be determined as well as the osmotic pressure second virial coefficient. The latter is a thermodynamic property that is a useful indicator of the solvent power.

Dynamic or quasi-elastic light scattering can provide information on molecular motions, such as the diffusional and hydrodynamic behavior as well as information on equilibrium properties. In this respect it is a more versatile experimental tool than static scattering methods.

Much of our effort has been devoted to developing the idea that dilute polymer solutions satisfy a corresponding states principle. Polymer solution properties, such as intrinsic viscosity, are a function of three variables: molecular weight, temperature, and solvent. Scaling theories suggest that these three variables can be combined into a single excluded volume parameter and that all dilute solution properties can be expressed as a function of this single parameter. This corresponding states idea holds considerable potential for simplifying and unifying the different approaches used in polymer characterization. We have tested these ideas by comparing theory with experimental data collected from small angle neutron scattering, light scattering, and quasi-elastic light scattering measurements. To date, satisfactory agreement has been obtained which suggests that the corresponding states approach is valid.

A state-of-the-art light scattering photometer was developed and used in the measurement of polystyrene SRM 1479 at room temperature. However, because of the thermal instability of the optical bench used in this system, measurements at the elevated temperature, required for ultra high molecular weight polyethylene, could not be made. Consequently, the optical bench has been redesigned to be thermally isolated from the heated cell. In addition, a stepping motor driven goniometer has been installed. The redesigned apparatus will now how the option for simultaneous static and dynamic light scattering measurements at elevated temperatures that are required for polyethylene.

Polystyrene solutions in the dilute region have been studied by dynamic light scattering experiments. The first cumulant, $\Omega(q)$, has been extracted consistently by either the cumulant analysis or the shape function analysis. It is found that $\Omega(q)$ approaches q^2 dependence as $qR_g << 1$ and q^3 dependence as $qR_g >> 1$ with a broad transition region. It is also found that the magnitudes

of the first cumulant at q^3 region changes from θ-solvent to good solvent condition. Inboth cases, experimental results agree better with theoretical calculations which use preaveraged Oseen tensor. It seems that either the analytical Gaussian model of equilibrium polymer chain distribution function or the Oseen tensor hydrodynamic interaction has to be improved.

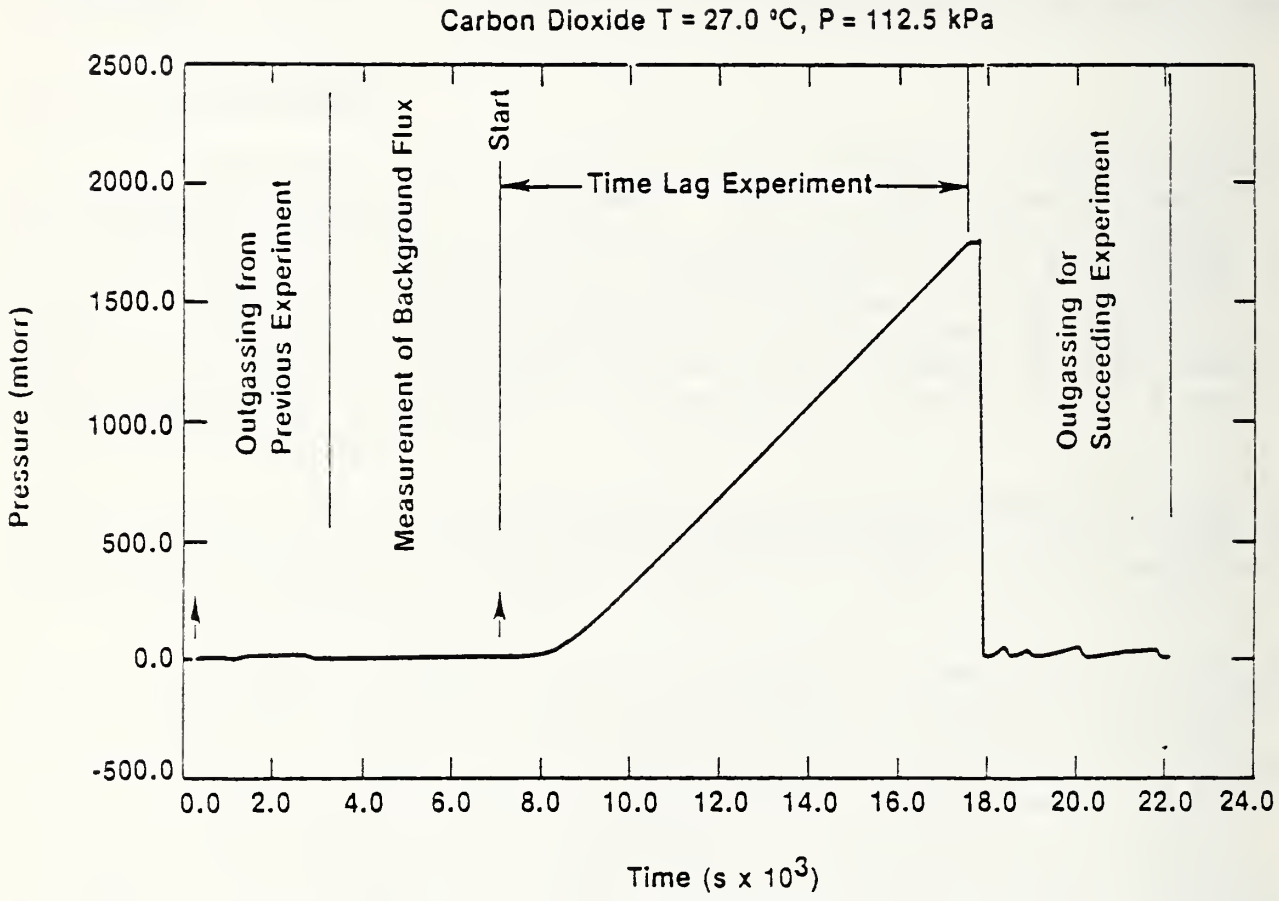
Carbon Dioxide T = 27.0 °C, P = 112.5 kPa
Pressure (mtorr)
2500.0
2000.0
1500.0
1000.0
500.0
0.0
-500.0
Outgassing from Previous Experiment
Measurement of Background Flux
Start
Time Lag Experiment
Outgassing for Succeeding Experiment
0.0 2.0 4.0 6.0 8.0 10.0 12.0 14.0 16.0 18.0 20.0 22.0 24.0
Time (s x 10^3)

Figure 1

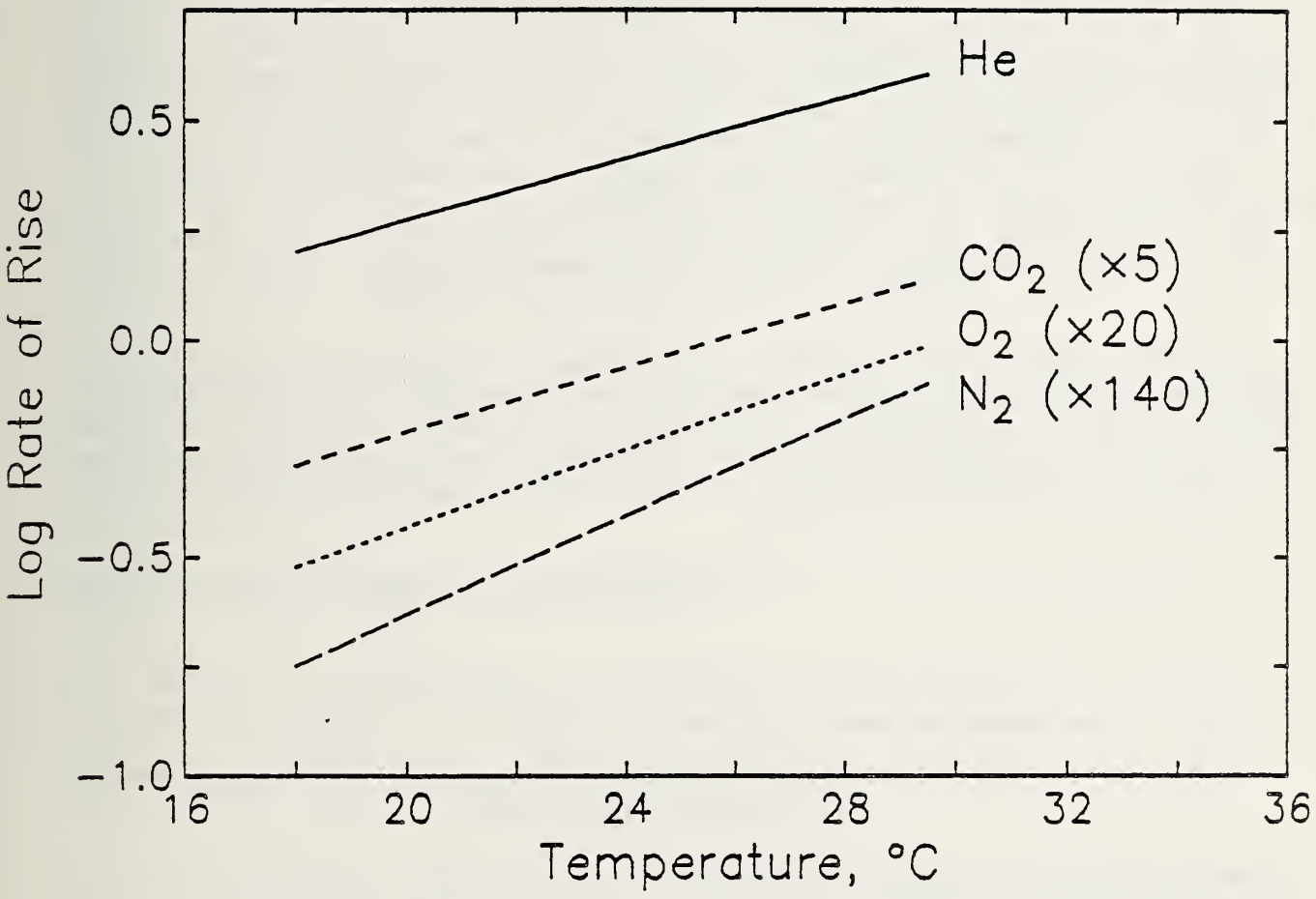
He
CO_2 (×5)
O_2 (×20)
N_2 (×140)
0.5
0.0
−0.5
−1.0
16
20
24
28
32
36
Log Rate of Rise
Temperature, °C

Figure 2

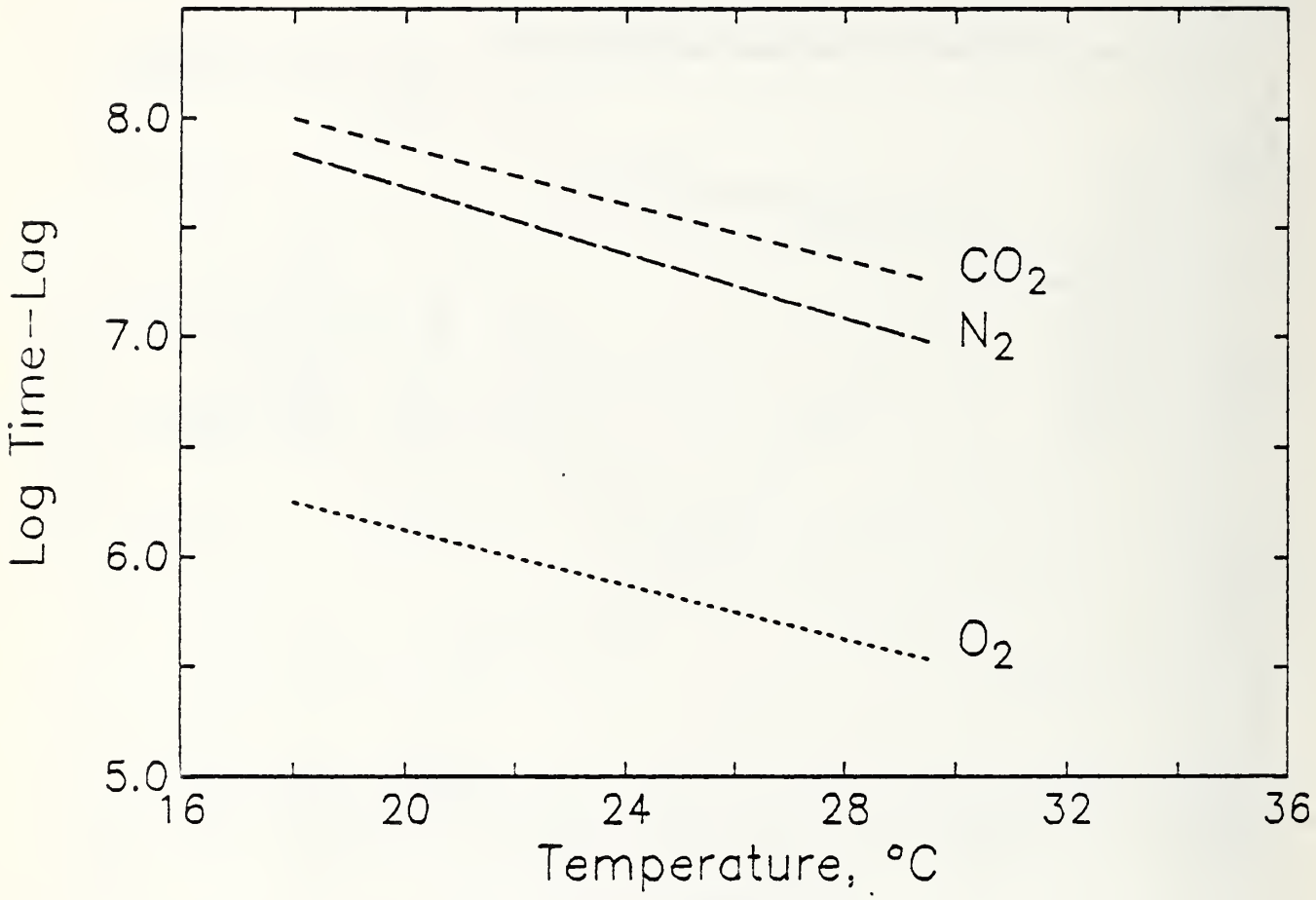

Figure 3

TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
Task 12135

The objective of this research is to contribute to health care through development of better performing materials and test methodology and standards appropriate thereto. Materials research and techniques are pursued with the goal of developing dental adhesive composite restorative materials of greater durability and wear resistance and improved base metal alloy alternatives to the costly gold alloy dental prostheses. Knowledge of the structure and physical chemistry of biologically important calcium phosphates is used to develop improved preventive dental techniques. Improved test methodology is sought for characterization of the surfaces of surgical implant materials for defining the interactions that occur thereon. Means for characterizing the porosity of low modulus, polymeric, medical implant materials are sought.

Dental research directions in support of the objective are established collaboratively with the American Dental Association, the National Institute of Dental Research, and the Department of Defense Medical R&D Command. Medical materials research is guided by close interaction with the Food and Drug Administration's Bureau of Medical Devices and the ASTM F-4 Committee (Medical and Surgical Materials and Devices).

Dental Composite Chemistry and Development
Subtask 1 of Task 12135

G. M. Brauer, J. M. Antonucci, J. W. Stansbury, J. M. Cassel, R. L. Bowen[1], H. Argentar[1], D. N. Misra[1], T. Chen[2], E. E. Toth

[1]Research Associate, American Dental Association.
[2]Guest Worker, Food and Drug Administration.

Current efforts are directed toward upgrading the quality of composite restorative materials with regard to color and storage stability, toxicity effects, adhesiveness, and durability.

Chemical and photo (visible and ultraviolet) polymerizations of experimental resin formulations in which the monomers, the amine or other type accelerator, and the initiator are varied are being compared for development of dental resin systems having enhanced storage stability and which yield dental composite restorative materials with improved color, chemical and mechanical stability, and are minimally toxic to the pulp. A number of mono- and dimethacrylate monomers that are bulkier in structure than BIS-GMA have been prepared for examination of their possible reduction in the shrinkage incurred on polymerization of the composite formulation. Various combinations of base resin, e.g., BIS-GMA, and new diluent monomers are also being investigated for this purpose. Experimentation with DSC has shown that the extent of polymerization (or residual unsaturation) in the highly cross-linked dental composite resin systems can be investigated by this means. Correlation of these results with oxidative stability and wear resistance of composites is planned.

Photochemical polymerization initiating systems that on the basis of their structure would appear biocompatible are being investigated. Means are being

TESTS, STANDARDS, AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
Task 12135

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sought to effectively incorporate into clinically initiated paste/paste composite formulations the non-amine type polymerization accelerators, such as ascorbic acid, that give composites with excellent color stability and biocompatibility when adsorbed onto the powder in powder/liquid systems. Amine accelerators which are esters of dimethylaminophenethanol and succinic, maleic, and acrylic acids have been synthesized and will be evaluated in composite resin formulations.

Continuation of the investigation of the effect of amines on the silanization of composite filler particles has shown that primary aliphatic amines are the most effective and aromatic and heterocyclic types the least effective catalysts. The solvent from which the coupling agent is deposited has also been shown to be an important factor with non-polar solvents, e.g., cyclohexane, yielding a higher degree of silanization of a more hydrolytically durable nature than that obtained with polar solvents, e.g., acetone.

At least one manufacturer is preparing on a commercial scale the semi-porous glass which was developed earlier in this laboratory as a means to achieving better reinforcement of the composite resin matrix by the filler component. The combination of an etched filler surface along with the more effective means for applying the coupling agent may provide a means for achieving more durable composite restorations.

Development of Adhesive Bonding Technique and Dental Cements
Subtask 2 of Task 12135

G. M. Brauer, R. L. Bowen[1], J. M. Antonucci, D. N. Misra[1], J. W. Stansbury, E. Cobb[2], J. M. Cassel

[1]Research Associate, American Dental Association.
[2]Guest Worker, Georgetown University Dental School.

Although effective bonding to enamel is presently achieved by means of acid etch treatments, similar treatments of dentin are contraindicated in tooth restoration procedures. An effective bonding procedure for use with dentin would promote more conservative tooth restoration procedures.

A series of so-called reactive adhesive formulations prepared by solubilizing selected elastomers in acrylic, methacrylic acid, or methacrylate ester monomers have been examined for their adhesiveness to mineralized tissue such as bone. Bond strengths after three months storage in water did not exceed 1.0 MPa, and this approach has been discontinued.

While the stability to water of the bonding to dentin with isobutyl cyanoacrylate is not satisfactory, the initial bond strength attained with this material is the highest achieved to date so far. Attainment of this high initial bond strength requires a cleansing of the surface of the dentin by a one percent citric acid pretreatment which may be too severe for the dental pulp. However, replacement of the acid by pretreatment of the dentin surface with dilute sodium citrate solutions gave joints with excellent bond strength. To mitigate the response of the pulp to such materials, we have been examining the use of isotonic surface cleansing solutions to which we have incorporated mordanting agents as a means of altering or increasing the mineral surface to adhesion. Currently, we are examining the application sequentially of two coupling

agents, each applied from a volatile solvent. The coupling agents apparently penetrate into the altered dentin layer and provide bound molecules that can copolymerize with the resin of the composite material applied subsequently. The dentinal tubules do not appear to be enlarged or filled to any significant depth with the adhesive or polymeric material, so the very high bond strengths currently being achieved are not the result of mechanical attachment via resin tags penetrating the tubules and insulting the pulp. Other coupling agents that are designed to react with labile hydrogen groups in dentinal collagen have been synthesized and will be evaluated, e.g., monomers with pendant isocyanate and aldehyde groups.

Zinc oxide-eugenol (ZOE) cements, because of the excellent biocompatibility of the hardened material, are widely used in dentistry. However, their comparatively low strength and lack of resistance to wear and disintegration along with their inability to adhere well to acrylic restorations or to mineralized tissue are recognized as significant deficiencies. Further, their inhibiting effect on the free radical polymerization of acrylic resins and to a lesser extent dental composites with which they may be placed in contact, reduces their usefulness. In the past, substitution for the eugenol component which inhibits polymerization has usually resulted in cements possessing poor physical properties.

Currently, we are investigating cements in which the liquid ingredients are esters of vanillic acid or its isomers containing o-alkoxyphenol or other groups capable of forming chelates with multivalent salts. Neither vanillic acid nor its common isomers are liquids at room temperature, which is a prerequisite for conveniently preparing a cement by mixing the chelator with a metal oxide. The hexyl ester of vanillic acid (HV) which we have synthesized is a liquid at room temperature. The hardening reaction of this ester with zinc oxide is much too slow for dental application, but by incorporating a second chelating component such as o-ethoxybenzoic acid (EBA), we have increased the reaction speed to a useful range. The resulting cement has high strength, does not inhibit dental resin polymerization, and adheres strongly to acrylic resins and composites even after prolonged exposures in an aqueous environment. Incorporation of dimethacrylates in the formulations allows a rapid cure of such "composites" in the presence of an initiator-accelerator system and yields cements with good physical properties. Further improvement in these properties is being sought through the incorporation of divanillates that we have synthesized for their cross-linking potential.

The complete absence of inhibition to methacrylate resin polymerization of HV-ZOE cements has many advantages:

It allows incorporation into the cement mix of polymerizable monomers. By suitable techniques such as redox polymerization, these monomers can be cured to strengthen the cement and to yield cross-linked, multiphase, or interpenetrating networks which are less soluble, more degradation resistant than the presently available cements.

A portion of the cement when used clinically as a temporary restoration can be retained as a base for an acrylic resin restoration. This should shorten the time necessary for placing the permanent restoration. A complete reexposure of deep cavities is also avoided, which should reduce irritation of the dental tissues during the clinical procedure.

Wear Resistance and Mechanical Properties of Dental Materials
Subtask 3 of Task 12135

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[1]Guest Worker, Georgetown University Dental School.

A silver staining technique developed and applied initially last year in a study of the mechanisms of wear in dental composite restorations is continuing to yield promising results. By this means, the creation of microdefected subsurface damaged regions is readily observed in both *in vivo* and *in vitro* worn specimens. This technique has been used to examine the attack of various solvent media including aqueous organic systems on dental composite materials and when combined with hardness measurements has shown that establishing solubility parameter data on dental composite resins is important in investigating the mechanisms of degradation that influence wear resistance.

Experiments with small angle x-ray scattering to examine the shape of the microdefects created in subsurface damage regions of worn composites are in progress. The necessary theoretical background for this application has been completed, and the analyses of *in vitro* compression fatigued composite specimens are being compared with that of *in vivo* exposed materials. Preliminary results indicate a more isotropic-shaped defect in the clinical specimen with the conclusion that compression fatigue may not be a dominant factor in the *in vivo* wear process.

With our *in vitro* pin-on-disc accelerated wear test, we are continuing to advance our state of knowledge of composite wear. Analysis of composites subjected to wear over a range of normal stress levels from 2.5 to 20 MPa have revealed that abrupt changes by a factor of roughly two in wear rate occur during the course of wear. This is shown in figure 1 where we plot the depth of the wear track as a function of the cycles of exposure of the dental composite disc to a stainless steel pin. We attribute this result to an initial wear region dominated by an adhesion process followed by a region in which subsurface damage increases to a point where breakdown occurs from fatigue. Only specimens with wear terminated in the second region of wear show subsurface damage by the silver staining technique. Subsurface damage caused by diffusion of solvents in dental composites is being correlated with *in vitro* wear performance using the silver staining technique. The extensive deterioration in the *in vitro* wear resistance of a commercial dental composite previously exposed to ethanol-water solutions is indicated in figure 2 where we plot the depth of wear track generated by a stainless steel pin in a dental composite disc after each of the first five revolutions of the disc. This type of information provides clues to efforts here and in industry to develop more durable plastic composite restorative materials.

Porcelain Fused to Base Metal Alloys and Dental Ceramics
Subtask 4 of Task 12135

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A major cause of failure in porcelain fused-to-metal restorations involves cracking or delamination of the porcelain veneer. This is thought to arise primarily from residual stress trapped within the system during cooling from the firing temperature. These stresses originate in the differences in thermal expansion and stress relief characteristics of porcelains and alloys.

To determine optimum combinations of thermophysical properties for porcelains and alloys, a multifaceted investigation of properties is in progress: (a) coefficients of linear thermal expansion are being determined for several brands of alloys and porcelains which have been subjected to one through seven laboratory firing cycles, (b) viscous flow characteristics are being measured, and (c) measurements of mechanical properties as a function of temperature are planned. Stress is being evaluated via a combined experimental and theoretical determination of the change in gap of porcelain veneered split metal rings using experimentally determined thermophysical properties. Correlation between measured and predicted gap changes provide the necessary information to calculate stress at any position within the ring. Ring and porcelain dimensions have been chosen to be somewhat representative of a crown.

Thermal expansion data for a number of porcelains have now been acquired and reported on. In addition to this property, information on the temperature dependence of the shear viscosity for a number of dental porcelains has been developed and reported on. A parametric study on the importance of parameters such as the temperature dependence of the elastic modulus and Poisson's ratio was conducted and discussed. Results of the latter study show that Poisson's ratio is not a critical factor in determining stress or strain within a system. The elastic modulus, however, is an important factor in stress. A 40 percent increase in modulus of porcelain can result in a doubling of stress within porcelains.

One area of particular concern involves the influence of transition bonding zones between alloy and porcelain on experimental determinations of stress and strain. Theoretical calculations of the effects of differences in thermal expansion showed that interfaces as thick as 20 μm, with differences in expansion (from that of porcelain or alloy) as large as 10×10^{-6}/°C, are not capable of producing significantly measurable effects at the 2.5 percent level of detection, provided the porcelain to alloy thickness ratio is one. Experimentally, this is the condition achieved in porcelain fused-to-metal split rings. A paper was presented on this at the 1981 IADR/AADR meeting. It should be noted that the analysis used in this case is useful for predicting strain but is not capable of providing detailed stress analysis.

The theoretical approaches for calculation of stress in split metal rings has been refined; the finite element program has been reconstructed to include a finer mesh and definition of elements near edges (for edge effects) and to

include viscous relaxation of porcelain. Stepwise numerical calculations, incorporating viscous flow, have been made using analytical models and have shown improved agreement with experimentally determined gap changes of composite rings.

The development of "Gel-route" technology for application to dental porcelain and investments has continued. "Gel-route" technology, in which the desired composition of a solid phase is obtained by mixing aqueous solutions rather than by preparing a glassy frit has several advantages over conventional porcelain frit production; among them are lower capital and labor costs for production and less supply dependence on scarce raw materials. New compositional and heat treatment variations are being tested. Porcelain frits suitable for metal-ceramic applications have been made that mature in a 12 minute air fire at temperatures 50 to 175 °C lower than the current lowest-fusing commercial metal-ceramic porcelain. The strength, thermal expansion coefficient, and solubility (in four vol percent acetic acid solution at 80 °C for one week) compare favorably with currently available materials.

A device has been constructed to measure the force of investment setting that uses the nondestructive setting-ring test that had been developed for the measurement of both setting expansion and temperature set. Preliminary results using one phosphate bonded investment indicate that the force of setting is over four times greater with a wet asbestos liner than with an identical dry liner. It also increases slightly with increasing silica concentration in the liquid and with decreasing liquid-to-powder ratio. Most of the force, as well as expansion and heat evolved on setting, occurs after a hard set is achieved.

A patent on a microporous glassy filler for dental resin composites has been issued. Another patent on the gel route preparation of dental porcelain frit has been filed. Several dental companies have shown interest in our gel-route prepared frit.

Dental Casting Alloys
Subtask 5 of Task 12135

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Problems of cost and limited availability have been encountered in recent years for commercial dental casting alloys based on gold or cobalt, and some concerns continue to surface for the toxicity of nickel-based alloys, although there appears to be very limited evidence that this is indeed a problem except where a skin sensitivity to nickel has been established.

Earlier in this laboratory, we prepared the first titanium-based dental castings using a titanium/copper alloy. These castings were made under argon with our conventional casting equipment. During the past year, we have designed and constructed an electric-arc furnace for melting and casting titanium alloys using conventional dental investment molds heated in the usual manner. The initial castings with this equipment demonstrate that this technique is feasible and may be more economical than the present induction centrifugal methods used

in commercial dental laboratories. We have cast both the relatively low-melting titanium/copper alloys and pure titanium in the form of typical test castings. Much more information is needed relative to dimensional accuracy, mold materials, porcelain-metal bonding, mechanical properties, and casting techniques.

A study reported from this laboratory two years ago showed that single crowns of base metal alloys could be cast to sufficient oversize to produce fits which would be considered as clinically acceptable. However, the question remains as to whether the same techniques would work for multiple unit castings. A series of experiments were, therefore, conducted to investigate the fit of multiple unit, fixed partial dentures on a double die system which consisted essentially of combining two single dies of the pattern previously used. Results to date have shown that although some distortion of geometry occurred under all conditions investigated thus far, the use of plastic runner bars should be avoided and a bench setting technique with an all wax system produced minimum distortion.

A pilot study attempting to join individual base metal alloy castings by soldering has been unsuccessful to date. Alloys that performed best in our castability study often contain constituents that preclude reliable joining by conventional soldering methods. Some manufacturers who have been in contact with NBS are aware of the problem and are expending effort in this regard to improve their products.

A simple, objective castability test which does not require sophisticated measurement devices would be of benefit to both users and developers of dental alloys. For this purpose, we had previously developed a technique that employs the use of a pattern of polyester mesh, waxed, sprued, and invested by standard dental laboratory practices. Following burnout of the pattern and casting of the alloy, the number of completed cast pattern segments provides a measure of castability. Results reported to the 1981 IADR/AADR meeting indicate that the test is sensitive to a number of processing variables such as casting temperature, mold burnout temperature, and investment brand. This development is being continued with a view toward evaluation of these parameters for a number of alloys and to make the test more sensitive to them.

Clinical and Laboratory Investigation of Dental Amalgams
Subtask 6 of Task 12135

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The deterioration of amalgam restorations often begins with a slight extrusion from the cavity. This extrusion appears to be caused by some internal transformation which produces an expansion of the alloy. Recent experiments indicate that the presence or absence of zinc in the amalgam has a pronounced effect on the expansion, particularly in the higher temperature range (60 °C). Metallographic and x-ray diffraction studies have thus far been unsuccessful in identifying the cause of the expansion. Detailed metallographic studies of the reacted alloy powders are now underway, and further studies of the amalgams are to be initiated in the near future using a transmission electron microscope (TEM).

In a cooperative study with the University of Virginia, it was found that increasing the zinc content (1) increased the mercury/alloy ratio needed to obtain a proper consistency of mix, (2) increased the residual mercury content of the amalgam, (3) decreased dimensional changes that occur during hardening, (4) increased the compressive strength, and (5) decreased the creep.

Long-term clinical observations are continuing, and an attempt is being made to determine the causes of success or deterioration.

Dental Chemistry and Preventive Dental Treatments
Subtask 7 of Task 12135

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[1]Research Associate, American Dental Association

The objective of this project is to develop and apply fundamental information on the solubility and crystallographic structure of biologically important calcium-containing phosphate compounds to the development of improved dental caries preventive techniques. Important portions of this effort are concerned with (1) development of physico-chemical models of the caries process to include insight into the mechanisms by which impurities and defects are incorporated onto tooth enamel, and (2) application of solubility phase diagram analysis and kinetic data to the development of more effective enamel acid etch bonding treatments and improved topical fluoride procedures.

Continued progress has been made in developing a new procedure for studying the mechanism by which enamel crystals grow and react with fluoride. Advances were made in methodology, using rats as an animal model, as well as in collecting new experimental evidence. Considerable in vitro evidence has accumulated over the years that an acidic salt, octacalcium phosphate, is formed first in the developing enamel and then is converted to the final form, a basic salt, hydroxyapatite. Fluoride ions facilitate this conversion. Through the use of radioactive phosphorus, a promising nw method was developed which measures the relative amounts of the acidic and basic calcium phosphates reproducibly in the rat incisor. The experimental results support the view that an acidic calcium phosphate is a precursor in tooth mineral formation, and they bring us a step closer toward understanding how fluoride in drinking water during tooth formation acts to reduce dental caries. These experiments were carried out in the animal facilities of the ADA Research Institute in Chicago.

Carbonate is a major impurity in tooth mineral, and its presence there is generally thought to enhance the solubility and, therefore, the caries susceptibility. Solubility measurements were carried out on synthetic and natural tooth mineral in the presence and absence of carbon dioxide in the atmosphere. Contrary to expectations, carbon dioxide lessened the solubility of tooth mineral. These results indicate that the effects of carbon dioxide in the atmosphere and of carbonate in the mineral on enamel solubility need to be examined more carefully in order to determine their true roles in tooth decay.

Studies are being carried out on the chemistry of the tooth decay process by using ultramicro techniques. Small wells are drilled into quarter-millimeter thick tooth sections. These sections are then placed into cariogenic solutions, and the chemical events taking place within the wells are measured. These well are only about 0.1 mm in diameter and are barely visible to the unaided eye; since a complete chemical analysis of the solution within such wells must be obtained, it can be seen that the procedures involved are exceedingly delicate. Our recent work has shown that the solution within the wells is saturated with respect to enamel mineral and that the response time is relatively slow compared to the rates of change in the environment of the tooth due to normal dietary fluctuations. These results require substantial modification of the caries models used in the past. Work of this type may reveal steps within the process that can be artificially slowed so as to reduce the rate of formation of cavities.

It is predicted on the basis of theory that neutral salts such as NaCl or KCl can act as acids or bases, thereby strongly affecting the caries process, when the surface of the tooth holds either a positive or a negative ionic charge, respectively. This theory was tested in bench scale experiments and was found to be valid. The full implications of these results are not known, but the importance of neutral salts in the caries process warrants careful consideration in the future.

A previously reported topical fluoridation procedure which incorporates more permanently-retained fluoride into the tooth than the treatments now in use has been moved closer to clinical application. During the past year, several new modalities of treatment were tested in the laboratory and were found to be effective. Substantial progress was made in preparing for a clinical study of this procedure. This trial should go a long way toward confirming or refuting the commonly held hypothesis that increasing the fluoride content of enamel increases its resistance to decay.

We have determined the structures of several calcium phosphates with emphasis on layer-type and highly hydrated structures. Two of these compounds, $CaBr(H_2PO_4)\cdot 4H_2O$ and $CaI(H_2PO_4)\cdot 4H_2O$, are of a new type in that they contain planar calcium phosphate sheets, a structure that has been found only once before. They provide a plausible structural model for calcium phosphate complexes in concentrated solutions. The structure of the compound, $Ca_2KH_7(PO_4)_4\cdot 2H_2O$, which contains a corrugated sheet arrangement of calcium and phosphate ions, was determined, and work is in progress on a compound which apparently contains a calcium-phosphate sheet interlayered with urea molecules.

Development of Improved Field Dental Composite Restorative Materialsfor Military Personnel

Subtask 8 of Task 12135

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Field use of dental composites would be significantly aided by development of composite systems that were more easily placed and had greater storage stability.

As with all composite restorations, there is also the need for improved marginal adaptation in the hardened materials in order to prevent the microleakage that can reduce the effective lifetime of restorations.

In this current year, we have extended our investigation into the roles of polymerization shrinkage, coefficient of thermal expansion, nature of the filler, and properties of diluent monomers in the phenomenon of microleakage. Based on radiotracer analysis applied to class V restorations placed in extracted caries-free teeth that are subsequently thermocycled, we find the coefficient of expansion of a particular composite to be less important in microleakage prevention than is the influence of diluent monomer on the overall polymerization shrinkage. Measurements in which hydrophylic diluent monomers have been incorporated as a means of counterbalancing the polymerization shrinkage through increased water sorption and the resulting expansion do not appear to support this approach to solving microleakage problems.

A silver staining technique being used to investigate the mechanisms of wear of dental composites will be examined for its ability as a more sensitive means of assessing microleakage than the radiotracer technique we have been employing. The possibility of producing composite systems with low polymerization shrinkage and with a more hydrophobic character than that of currently available materials is to be investigated.

Adhesion and Surface Coverage of Synthetic Polymers on Solid Substrates
Subtask 9 of Task 12135

R. E. Dehl, W. H. Grant

Two aspects of the adhesion of polymers to surfaces are of great importance in their many commercial applications as protective coatings, namely, (1) the energy of adsorption of individual polymer molecules on the surface, which determines the adhesive strength of the film and (2) the extent of surface coverage by the polymer, which determines the effectiveness of the adherent film in protecting the underlying substrate from chemical attack. We are investigating this important problem by the use of radiolabeled polymers to study the adherence of the film. A measure of the energy of attachment of polymers adsorbed on solid surfaces is the rate at which they become detached when the polymer-coated substrate is placed in contact with a suitable solvent. The results of previous NBS studies, using radiolabeled polystyrene to detect the amount remaining on the surface, indicate that the rate of desorption decreases with increasing molecular weight of the polymer and with the amount of polymer initially adsorbed.

We have recently discovered that the rate of desorption of polystyrene from a chromium oxide surface into cyclohexane solvent depends not only upon the amount adsorbed but also upon the way in which a given amount of polymer is adsorbed. If the time spent in adsorbing a given amount (A) of polymer is very long or if the surface is first adsorbed to a higher level B > A, the subsequent rate of desorption into solvent from level A is much slower than if level A is attained quickly before desorption is begun. We feel that the most likely explanation for these phenomena is that the surface has at least two types of adsorption sites which differ in their energy of attraction for polymer molecules. We know that some adsorbed polymer exchanges with dissolved

polymer during the adsorption so that a very slow adsorption allows the higher energy, less easily desorbed sites to fill with polymer at the expense of the lower energy sites. Similarly, adsorption to a higher level B > A and desorption back to A leaves the surface with a higher fraction of high energy sites occupied than if the sites are quickly and randomly filled up to level A. The effects of surface roughness and other surface properties will be examined for their effect on the desorption rate of adsorbed polymers.

Arrangements have been finalized to begin an ESCA investigation with Center for Materials Science instrumentation that will endeavor to determine the usefulness of this technique for determining the homogeneity of polymer coatings applied to solid surfaces.

Characterization of Porosity of Porous Implant Materials
Subtask 10 of Task 12135

R. E. Dehl, W. H. Grant, J. M. Cassel

The use of porous synthetic implant materials to serve as a scaffolding for the ingrowth of natural hard or soft tissue is a procedure utilized to stabilize selected medical implants. Characterization of the porosity of these materials is very important, since the porosity governs their successful utilization. In cooperation with the Bureau of Medical Devices, Food and Drug Administration, we have concluded a survey of published information and current commercial material specifications and have performed mercury porisimeter measurements on polymeric (polyethylene) and a composite (graphite fiber immersed in polytetrafluoroethylene) implant material. The results clearly demonstrate the usefulness of the mercury porisimeter technique for providing a "fingerprint" characterization of the materials.

A study of the effect of precompression on the composite material has shown that precompression by a pressure 20 percent greater than that encountered by the material during a mercury intrusion experiment did not change the ensuing pore size distribution curve, as compared with a noncompressed sample. Deformation of the material at higher pressures sufficient to decrease the sample volume inelastically by 17, 33, and 67 percent changed the shape of the mercury intrusion curves significantly, indicating that the technique can be used to detect prior deformation of an unknown sample. In combination with a quantitative total void volume measurement, such as a continuation of Hg intrusion into the high pressure mode, this method can determine the fraction of total void represented by any pore size range of interest.

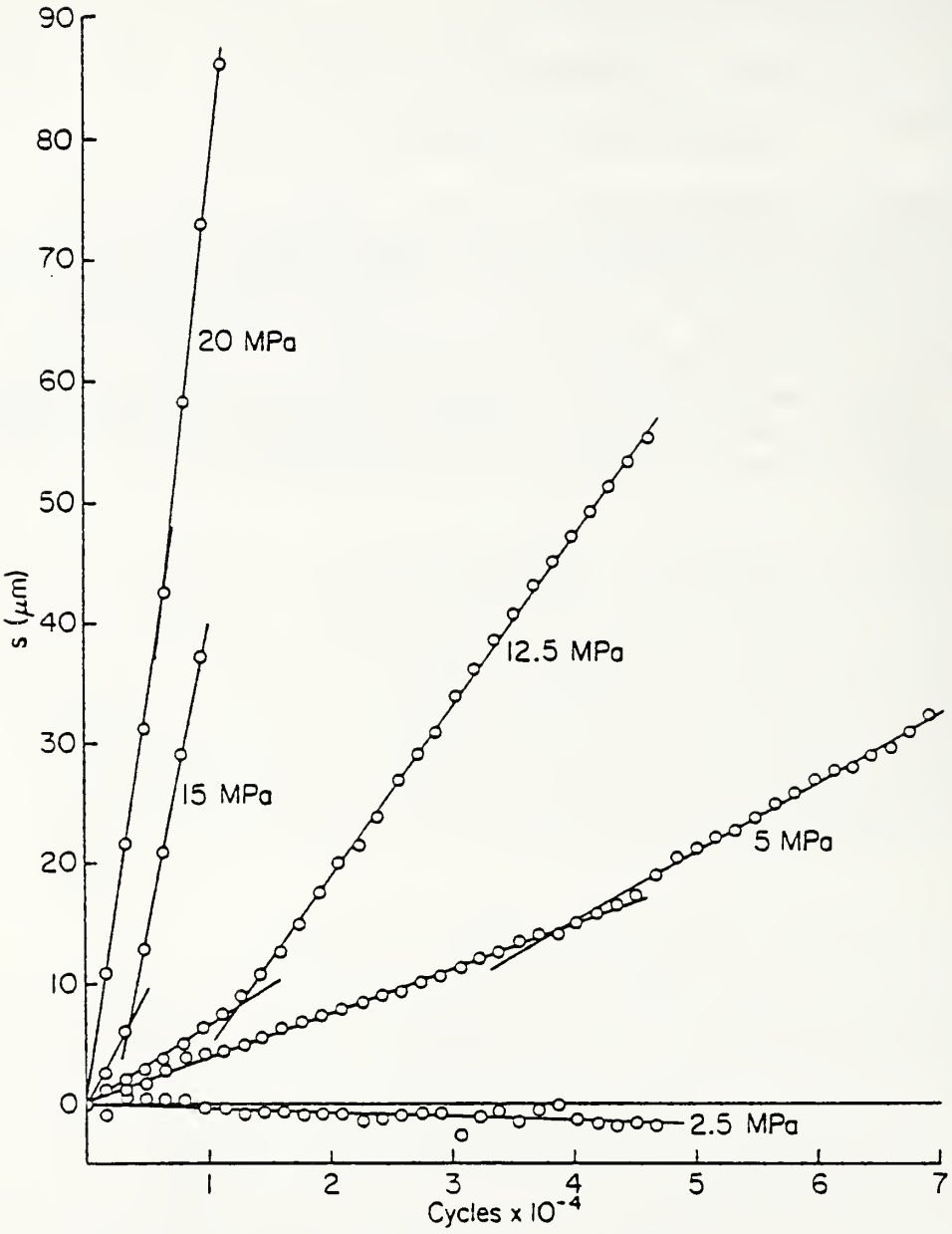
The accomplishment of this project's objectives will be of significance to the medical device industry, medical implant standards development, and, ultimately, the users of porous implant materials.

Dental and Medical Materials Standards
Subtask 11 of Task 12135

J. M. Cassel, J. A. Tesk, G. M. Brauer, N. W. Rupp[1]

[1]Research Associate, American Dental Association.

Active participation, from Task Force level to the role of Subcommittee Chairman, occurs in development of dental standards through ANSI MD 156, Dental Materials, Instruments, and Equipment, and ISO/TC 106, Dental Materials and Services. Development of medical implant standards is assisted by serving in roles of Polymeric Materials Chairman and Task Force leadership in the efforts of ASTM F-4, Medical and Surgical Materials and Devices, as Chairman, USA TAG ISO/TC 150, Surgical Implants, and through participation in the Executive Committee of the ANSI Medical Device, Standards Management Board. Significant leadership input has been provided to both ISO committees in preparation for meetings in 1981.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Cycles x 10⁻⁴

Figure 1

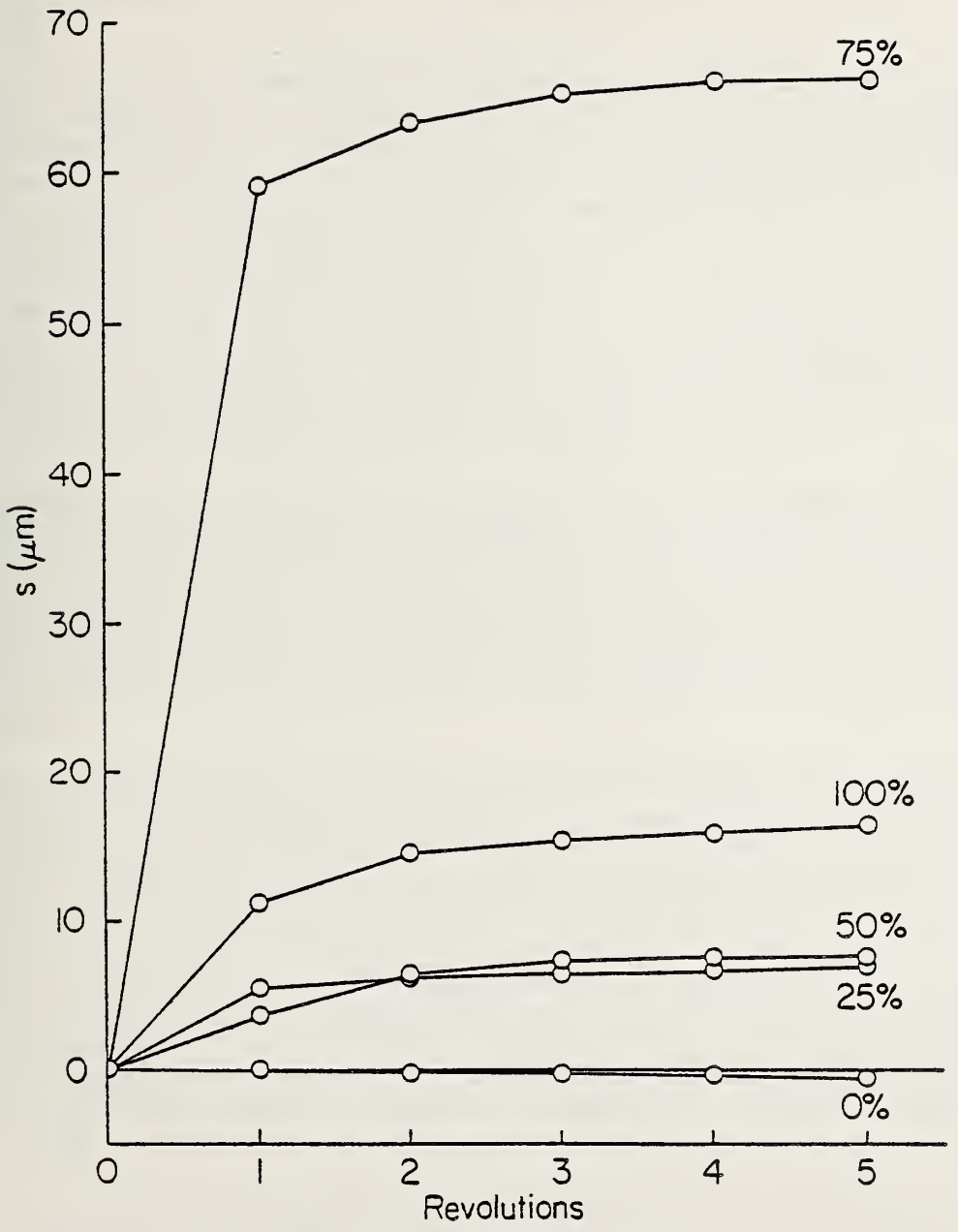

Figure 2

MECHANICAL DURABILITY OF PLASTICS FOR DESIGN AND USE
Task 12136

Polymeric materials increasingly are used in applications where long-term mechanical durability is critically important. The full exploitation of these materials would result in greater productivity through improved properties at lower costs. The realization of increased productivity is often limited by the lack of data and models upon which to design for long-term use. Thus, the lack of adequate test methods and data for evaluation of long-term mechanical performance not only restricts applications, but also leads to overdesign which results in more expensive items and limits weight savings. The substitution of polymer composites for critical materials in the aerospace industry has been limited for this reason. Evaluation and control of materials parameters that affect long-term performance should lead to more durable materials and, hence, reliable performance for the intended service life.

The objective of this task is to provide data, test methods, and standards for evaluation of long-term mechanical durability of polymeric materials. The approach is to identify and analyze principal failure mechanisms in these materials under mechanical stress in the use environment, to determine the effects of chemical structure and fine structure morphology on mechanical properties and failure processes and to develop constitutive relationships and models for mechanical properties as the basis for accelerated test methodology and lifetime prediction.

New activities have been initiated in glassy and composite polymeric materials. Theories have been developed to predict the rate of craze extension and stress relaxation in crazes at crack tips. The fracture energy of elastomer modified epoxy resin systems have been investigated to elucidate mechanisms of crack blunting in these composite materials. The identification of failure modes both at the fine structure and molecular level not only serves as a basis for models to predict long-term behavior but also may lead to quality control methods during processing. For example, incomplete chemical reactions during curing of composite materials has been shown to affect long-term mechanical performance. The extent of these chemical reactions during the cure process may be determined using spectroscopic techniques of nuclear magnetic resonance and Fourier transform infrared spectroscopy.

The National Bureau of Standards has established joint programs on mechanical durability with other Federal agencies which are fostering the application of polymeric materials in areas of national concern. A joint program with the Department of Energy is concerned with the mechanical performance of elastomeric seals in geothermal energy wells. The Bureau of Medical Devices of the Food and Drug Administration supports an investigation of relationships between the fine structure morphology of ultra high molecular weight polyethylene and the long-term mechanical properties of this material when used in medical implant devices. Improving the mechanical durability of fibrous network materials is the goal of a joint program with the Bureau of Engraving and Printing. In all of the above applications, there exists the need for test methods and standards to ascertain the physical limits of polymeric materials in various use environments. An outgrowth of a recent project with the Department of Transportation on mechanical durability of plastic shipping containers has been the development of a new test for environmental stress cracking. Optimal testing conditions are being identified for submission to the ASTM of an improved standard method for environmental stress-crack resistance.

Molecular Processes Associated with Mechanical Deformation and Failure
Subtask 1 of Task 12136

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The elucidation of molecular processes and structure changes accompanying mechanical deformation and failure not only provides the basis for development of test methods for long-term performance and quality control but also provides insight into the selection and design of materials with improved mechanical performance and durability. The semicrystalline structures found in most polymeric materials present significant challenges to characterization of molecular structure. New spectroscopic techniques involving ^{13}C nuclear magnetic resonance and Raman scattering are developed to elucidate molecular conformations in disordered material. Reorganization of polymer molecules during deformation affects mechanical performance and identification of the molecular processes involved and the resulting physical structures is the aim of the NMR studies.

Fourier transform infrared spectroscopy is used to determine the number of chain scissions produced per free radical measured during fracture in order to assess the role of free radical chain propagation reactions in the fracture process.

Spectroscopic Investigations of Mechanical Degradation of Polyethylene. Molecular processes associated with mechanical degradation of polymeric materials include chain rupture or scission. It has been postulated that chain rupture sites may be highly localized forming microvoids from which cracks may initiate leading to macroscopic failure [1]. The process of bond scission produces free radicals that may initiate many additional chain scissions before recombination to form stable chemical species. This would suggest that mechanical stability might be improved by the addition of free radical scavengers. The evidence for multiple chain scissions per free radical comes from comparisons of the number of free radicals generated during mechanical degradation measured by electron spin resonance and new end groups formed as determined by infrared spectroscopy [1]. Other estimates of the extent of chain rupture derive from viscosity-averaged molecular weight changes [2]. Number of chain scissions per free radical determined by viscosity measurements on mechanically damaged polyethylene is several orders of magnitude lower than the ratio evaluated from previous infrared data.

The previous infrared determinations were based on spectral differences between deformed and undeformed specimens [1,3]. Effects of molecular orientation, changes in sample thickness and surface texture, as well as differing void content could not be readily accounted for in these measurements. Another complication derives from the use of specimens with relatively high initial concentrations of end groups. For these reasons, we have carried out a detailed investigation of free radicals and chain scissions during mechanical degradation of polyethylene using electron spin resonance and Fourier transform infrared spectroscopy.

Measurements were made on tensile fractured polyethylene fibers, rods ground in liquid nitrogen, as well as an ultra high molecular weight polyethylene that was also mechanically degraded through grinding in liquid nitrogen. This last sample was of particular interest in that the undeformed material contained very few end groups. To circumvent spectral effects due to orientation, surface conditions, void content, and film thickness caused by the deformation, our approach was to cast a film of the deformed material from solution or the melt. Films for IR analysis were prepared from the reference material in an identical manner.

Spectral changes from new end groups were observed in the 900 to 1000 cm^{-1} region arising from vinyl groups, near 1375 cm^{-1} due to methyl groups, and in the 1700 to 1750 cm^{-1} region attributed to carbonyl groups. Increases were observed in the concentrations of the terminal vinyl, methyl, and aldehyde groups. The concentrations of new end groups are given in table 1 and compared to the free radical concentrations in table 2.

As evident from table 2, we find that the ratio of chain scissions to free radicals is lower by one to two orders of magnitude when compared to previous determinations. Our values are still approximately an order of magnitude larger than the viscosity-determined values [2]. We attribute the latter discrepancy to differences in molecular weight and the physical state of the samples used in the two studies. The discrepancy with previous IR studies [1,3] arises from sampling methods and the errors in the previous work associated with taking differences between relatively intense bands. In the case of the ultra high molecular weight polyethylene, no change was observed in the vinyl group concentration, even though the initial concentration of this species was extremely low.

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Table 1

Concentrations of Chemical Groups Formed During Mechanical Degradation of Polyethylene

Group	IR Band Freq. (cm^{-1})	Concentrations (No./cc) Ground PE Commercial	Ground PE UHMW	Fractured PE	Ref. 1
$RCH=CH_2$	909	$1.2 \pm 0.4 \times 10^{17}$	-	$1.3 \pm 0.4 \times 10^{17}$	3.4×10^{18}
RCH=CHR'	965	-	-	-	1.9×10^{18}
RCH_3	1,370	$2.2 \pm 1 \times 10^{18}$	$5.6 \pm 3 \times 10^{18}$	$7.3 \pm 4 \times 10^{17}$	11.8×10^{18}
RCHO	1,735	$3.7 \pm 0.5 \times 10^{17}$	$1.1 \pm 0.1 \times 10^{18}$	$1.9 \pm 0.6 \times 10^{17}$	4.6×10^{18}

Table 2

Chain Scissions Per Free Radical

	Ground PE Commercial	Ground PE UHMW	Tensile Fractured PE	Ref. 1
No. chain scissions per gram	$5.1 \pm 1 \times 10^{17}$	$1.2 \pm 0.1 \times 10^{18}$	$3.4 \pm 1 \times 10^{17}$	9.9×10^{18}
No. free radicals per gram	1.2×10^{16}	1×10^{17}	3.5×10^{15}	5×10^{15}
Chain scissions per radical	34 - 50	11 - 13	68 - 125	1,600

Examination of Drawn PET Fibers by ^{13}C NMR. Through a collaborative effort with the Firestone Tire and Rubber Company, several drawn PET fibers having different annealing histories at various constraints were investigated. Solid state ^{13}C NMR measurements were made at NBS on specimens furnished by Firestone and characterized by them with respect to mechanical properties, x-ray scattering, and density. The motivation behind this research was to determine whether solid-state ^{13}C NMR could: (1) clarify the concept and/or measurement of crystallinity in these fibers, (2) determine noncrystalline orientation, and (3) aid in relating molecular properties to mechanical properties.

Limited variable temperature data were obtained on non-spinning oriented samples. The rotation of a large number of aromatic rings about the 1,4 axis at frequencies near one kilohertz was observed in the temperature range of 130 to 150 °C. At room temperature, a few mobile aromatic rings were observed to rotate at similar frequencies. In these experiments, ring rotation is observed preferentially for those chains which have been oriented by drawing and/or annealing. The question of the morphological origin of these chains remains somewhat ambiguous since there has been no clear definition of crystallinity in the ^{13}C NMR results to date. Possible definitions of crystallinity in terms of lineshapes (spinning or non-spinning) or relaxation (T_{1C} or $T^{C}_{1\rho}$) have all given ambiguous results. X-ray results suggest that the crystallite block length is rather short (3.1 to 8.0 nm) and that percent crystallinities are low (20 to 40 percent). On the other hand, NMR results, particularly spinning lineshape analysis, suggest percent crystallinities in the range of 60 to 70 percent. We are considering using Raman or IR in future work on these samples to measure the gauche/trans ratio and how this ratio is related to the NMR and x-ray observables.

The methylene resonance in these non-spinning oriented samples is rather distinct from the rest of the ^{13}C NMR resonances. From this resonance, overall orientation can be determined. This analysis has not, as yet, been done in detail, but qualitatively, the following statements can be made based on the observed NMR lineshapes:

(1) Annealing at constant length improves the orientation of those chains which were already quite well aligned by the cold drawing. However, there is no appreciable change in the amount of new orientation of those chains whose direction deviated substantially from the draw direction.

(2) Annealing with free ends broadens the orientational distribution for the highly-oriented chains and significantly increases the number of poorly-oriented segments.

Examination by NMR of Morphological Changes in the Wet Beating of Cellulosic Materials. A collaborative effort with the Bureau of Engraving and Printing entails the examination of paper-related cellulosic materials. The background for this work was that in previous studies [1] it was shown that NMR could distinguish ^{13}C resonances associated with cellulose chains near the surface as opposed to the interior of an elementary fibril. Elementary fibrils are roughly 3.5 nm in diameter.

In paper making, cellulosic materials are soaked in water and then wet beaten. The latter process seems to plasticize the materials so that they will lay down to form a good paper. An important question concerns the fate of the elementary fibril during wet beating. It is known, for example, that wet beating cotton increases the amount of non-freezing water, while the fiber saturation point increases in wood pulp as a result of this process. So, in general, the amount of water intimately associated with the cellulose increases with wet beating.

For this project, a high speed water-tight rotor had to be designed which could spin stably at frequencies of at least 1.5 KHz. Such a rotor was designed, and data were obtained using dry, wet, and wet beaten samples of microcrystalline cellulose, Norway Spruce Kraft pulp, and purified cotton. The NMR results showed changes in the surface-carbon resonances on going from dry to wet samples. But no further changes were observed when going to the wet beaten material. Thus, it appears that wet beating does not break up the elementary fibrils to any significant (> 10 percent) degree. Some questions remain as to whether all of the carbons are being observed, but this problem cannot be addressed unless we acquire the ability to observe protons directly.

Reference:

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Study of Crystal Modification and Surface Area Changes in Mechanically-Deformed Ultra High Molecular Weight Linear Polyethylene. In FY80, we observed that cold (room temperature) drawn ($\lambda = 2.7$) ultra high molecular weight linear polyethylene contained a significant portion of the monoclinic crystalline phase along with the usual orthorhombic phase. This year, the amount of this phase was quantified using magic angle spinning (MAS) ^{13}C NMR. Furthermore, by taking advantage of magnetization diffusion of proton magnetization in solids along with the cross-polarization process between ^{13}C and ^{1}H nuclei, an attempt was made to measure the increase in going from the undrawn to the drawn LPE. The results, simply interpreted, indicated a significant increase (> 2x) in surface area in the drawn material. However, unambiguous interpretation awaits the ability to observe protons directly.

Spectroscopic Investigation of Disorder in Polyethylene. Characterizastion of order at the molecular level is fundamental to establishing connections between molecular structue and mechanical properties. Whereas the structure of crystalline material can often be deduced from x-ray scattering data, the details of molecular conformations in disordered material are not directly observable. In concert with suitable calculations of frequencies and intensities, vibrational spectroscopy can provide useful information on disordered polymeric materials. A case in point is the C-H stretching region of polymethylenes which is sensitive to both intra- and intermolecular order. In the Raman spectra of these molecules, there is a Fermi resonance interaction between the C-H bending and stretching vibrations, which depends on the state of the polymethylene chain. In the approximation that a gauche bond can be modeled by a decoupled CH_2 group, the Fermi resonance scheme for this system can be compared to that for the all-trans chain. The calculations indicate that a redistribution of intensity in the C-H stretching region occurs upon introduction or disordered structures in the all-trans chain. In particular, a band at 2935 cm^{-1} increases relative to a

band at 2850 cm^{-1} as the population of gauche bonds increases. This was demonstrated to occur for semicrystalline polyethylene of varying percent crystallinities and for melt polyethylene as a function of temperature.

Relationship Between Morphology and Mechanical Properties of Polyethylene. Subtask 2 of Task 12136

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The mechanical properties of semicrystalline polymers and their durability are related to the fine structure morphology. The work of this subtask is to determine these relationships for polyethylene, a widely used semicrystalline polymer. The morphology is determined by processing conditions and, to a lesser extent, by the use environment. An examination of processing conditions on morphology is an important aspect of the work. To improve our knowledge of the organization of polymer chains in bulk crystallized polyethylenes, studies have been carried out on solution crystallization at high temperatures. These conditions produce morphological features similar to those found in melt crystallized material with the advantage that detailed morphological examinations using electron microscopy may be made without subjecting the samples to harsh chemical treatments.

The Bureau of Medical Devices of the FDA supports investigations into the relationships between morphology and mechanical performance and durability of ultra high molecular weight polyethylene.

Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene. Ultra high molecular weight polyethylene (UHMWPE) is used in a variety of orthopedic joint prostheses. One factor which limits the expected lifetime of a prosthesis is the durability of the UHMWPE component. In clinical use, failure of the polymer component is not a result of wear alone but may occur through creep, fatigue associated with wear, or even fracture. The length of time between device implantation and clinical failure depends upon the time dependent mechanical response of UHMWPE to the clinical loading environment.

It is known that the properties of semicrystalline polymers are highly affected by such structure or morphology related features as degree of crystallinity, orientation, and spherulite size and texture. These features are determined by processing variables such as temperature and pressure histories used during fabrication of a finished polymer component. Under contract with the Food and Drug Administration's Bureau of Medical Devices, we are studying the relationship between morphology and the mechanical behavior of UHMWPE. An important consideration in this work is the determination of the material behavior variability which can be introduced by changes in the processing conditions and molecular weight so long as the molecular weight remains in what is considered to be the UHMWPE range, i.e., $M_w > 10^6$.

Protocols have been established for preparing compression molded sheets and solid cylinders of the UHMWPE. Features of the fine structure of both the raw polymer and the compression molded sheets and cylinders have been examined. Three aspects of the raw polymer have been studied: its morphological characteristics, its melting behavior, and its crystallinity. The polymer, as

received, is in its as-polymerized state and consists of fine particles. Because of its very high melt viscosity, both molded and machined prosthesis components made from it retain a memory of the particulate nature of the raw polymer. This was also true for specimens molded in our laboratory at temperatures as high as 90 K above the melting point. This observation emphasizes the importance of characterizing the structure of UHMWPE products, not only to determine their crystallinity but also to monitor those aspects of their morphology which are directly related to, and a consequence of, the particulate nature of the raw polymer. Since the nature of the shapes, sizes, and fine textures of nascent polyethylene particles vary depending upon the polymerization conditions, knowledge of the morphology of the raw polymer is a necessary aspect of the present study.

Differential scanning calorimetry (DSC) was used to examine the melting behavior and crystallinity of the raw polymer. The melting point was found to be between 413 and 414 K (140 to 141 °C). The percent crystallinity, as determined from the area under the melting curve, was 78 percent, which represents a value significantly higher than can be expected for the same material compression molded at temperatures above the melting point.

The mechanical behavior of the processed polymer has been examined for a variety of different deformation histories including single step stress relaxation, uniaxial creep, constant rate of strain, and cyclic loading. Stress relaxation and creep experiments have been done for material which was quenched from the melt (density = 0.923 g/cm^3), slowly cooled from the melt (0.935 g/cm^3), and slowly cooled followed by annealing at a temperature near the melting point (0.942 g/cm^3). Quenching of the polymer reduced the modulus at small strains by about a factor of two from that of the slowly cooled material, whereas annealing increased the modulus only by about 20 percent. One interesting feature of this material is that unlike lower molecular weight polyethylenes, in the quenched or slowly cooled state it does not exhibit the phenomenon of necking during a creep or constant rate of elongation experiment. However, upon annealing necking does occur.

The uniaxial creep behavior of the quenched and slowly cooled materials has been mapped for stresses in the range from nine to 27.5 MPa and time of from 10^2 seconds to 10^7 seconds ($\sim$ one/year). Although the quenched material is more compliant than the slowly cooled UHMWPE, the maximum stretch attainable was essentially the same for both ($\lambda \sim 6.0$). This is significantly less than is achievable in lower molecular weight polyethylenes which neck and then cold draw. The creep response of the annealed material was found to be very nearly the same as that of the slowly cooled polymer.

The cyclic fatigue behavior has been studied for two different UHMWPE samples which, based upon intrinsic viscosity measurements, have molecular weights of $M_w \sim 4.5 \times 10^6$ and 2.5×10^6. Tests were carried out at different levels of stress and frequency, and it was found that the fatigue lifetimes of both samples decreased with increasing test frequency. This behavior is the opposite to that for lower molecular weight polyethylenes ($M_w < 3 \times 10^5$). Further, it was found that the lifetime of the material having the lower molecular weight was about 30 percent higher than that having the higher molecular weight. This behavior is also unlike that of the much lower molecular weight polyethylenes

where the fatigue lifetime generally increases with increasing molecular weight. Sorting out the respective influences of molecular weight and density (fine structure) will require a comparison of both high and low molecular weight polymers having similar densities.

We have also begun to characterize the environmental stress crack resistance (ESCR) of the UHMWPE polymer prepared under varied processing conditions. The experimental technique being used to evaluate the ESCR is the same as that recently developed by us for application to other ethylene-based plastics. Preliminary results indicate that the ESCR is greatest for the slowly cooled material and least for the annealed UHMWPE.

The Morphology of Compression Molded Ultra High Molecular Weight Polyethylene (UHMWPE). The work described below is part of a continuing project sponsored by the FDA and whose objectives are to characterize the mechanical properties of UHMWPE and to examine the relationships between these properties and the morphology of the polymer. These relationships are of particular interest to the FDA because numerous components of artificial orthopedic implants (e.g., hip cups, tibial plateaux) are made from this polymer.

We have previously reported that sheets of UHMWPE (Mol. Wt. $\sim 4 \times 10^6$) which were compression molded at 200 °C and then slowly cooled to room temperature did not exhibit any necking when stretched uniaxially at a strain rate of 0.02/min up to the breaking strain. The density of the undeformed sheets prior to deformation was 0.936 g/cm^3. The absence of necking contrasts with the behavior of lower molecular weight linear polyethylene. More recently, the recovery of samples from uniaxial deformation to various strains below the breaking strain has been examined. The sheets exhibited considerable recovery. For example, sheets were stretched at 37 °C and at a strain rate of 0.02/min to strains of 0.25, 0.5, 1.0, 2.0, and 3.0, respectively. They were then released and allowed to cool to room temperature under ambient conditions. The corresponding residual strains after 24 hours at room temperature were 0.06, 0.12, 0.34, 0.92, and 1.15.

Wide angle and small angle x-ray diffraction patterns were obtained from the samples originally stretched to strains of 1.0, 2.0, and 3.0 at 37 °C. The x-ray beam was normal to the stretching direction. In the case of the wide angle patterns, the changes associated with increasing residual strain in the released samples were characterized by a progressive intensification of the 200 arcs in the equatorial region. Correspondingly, the 110 arcs, which were split about the equator, tended to be closer to the equatorial direction with increasing residual strain. In addition to the reflections associated with the usual orthorhombic unit cell of polyethylene, all three samples exhibited fainter reflections characteristic of a metastable polymorphic form of polyethylene, which form has been variously described as being monoclinic or triclinic [1]. The main feature exhibited by the small angle diffraction patterns from the same three samples was that as the residual strain increased, the patterns became more clearly "four-pointed" in character. This latter feature indicates the occurrence, between crystalline and disordered regions, of interfaces which are appreciably inclined relative to the stretching direction. In addition, the samples originally stretched to strains of 2.0 and 3.0 exhibited a central horizontal streak indicating the presence of long and comparatively narrow voids whose long dimension is oriented parallel to the stretching direction.

Examination of the samples mentioned in the previous paragraph in a scanning electron microscope indicated that although they did not exhibit any macroscopic necking when originally strained, stretching did not occur uniformly throughout each sample. The manifestation of nonuniform deformation was evidenced by the occurrence of regions which exhibit an apparent "fibrillar" appearance. These regions of higher deformation, in which the "fibrils" were oriented parallel to the stretching direction, were interspersed between regions of lower deformation which exhibited no evident fibrillar character. It remains to be determined whether this nonuniform deformation is associated with the memory, which the molded samples retain, of the grain-like character of the constituent particles of the raw UHMWPE polymer. This matter is currently under investigation.

The Habits of Polyethylene Crystals Grown From Solution at High Temperatures. The two main objectives of this investigation have been the following. First, to seek appropriately "poor" solvents from which chain folded polyethylene crystals could be grown which exhibit {110} and {200} lateral faceting and preferential growth parallel to the b-axis (i.e., axial ratios B/A > 1.33*) at temperatures which approach and overlap the temperature range (∿ 118 to 130 °C) in which the polymer crystallizes isothermally in the form of axialites and spherulites upon cooling from the molten state. Second, to characterize the lateral growth habits and conformations (non-planar character, e.g., hollow pyramidal or variously curved) of crystals having B/A > 1.33. Interest in the morphology of such crystals and its dependence on molecular weight and crystallization temperature stems from their potential usefulness as models for the experimentally less accessible constituent lamellae in the various axialitic and spherulitic structures which are formed in bulk (melt) crystallized polymer [2]. It has long been known that the preferred growth direction in the radiating lamellae in polyethylene spherulites is parallel to their b-axis. Notwithstanding the new insights provided by Olley, Hodge, and Bassett [3], the origins of the twisting of the lamellae in the spherulites as well as other aspects of the morphology of these lamellae remain obscure.

Using dodecanol as a solvent and two polyethylene fractions, Fraction I (Mn = 11400) and Fraction II (Mn = 28900), the highest temperatures at which crystallization has been achieved to date from 0.01 percent solutions have been 115 °C (Fraction I) and 120 °C (Fraction II), at which temperatures crystals having an axial ratio B/A ∿ 6.0 were formed. Examination of crystals of both fractions grown at 105 °C and above revealed that in addition to the fact that in both cases higher crystallization temperatures yielded crystals with a higher axial ratio, for given crystallization temperatures in the range 105 to 115 °C, crystals of the higher molecular weight fraction exhibited a smaller axial ratio. For example, the axial ratios of crystals of Fractions I and II grown at 115 °C were ∿ 6.0 and ∿ 2.4, respectively. This effect indicates that the axial ratio and, hence, ratio of the growth rates perpendicular to the {110} and {200} planes are governed primarily by the undercooling ΔT.

Various "self-seeding" procedures are being explored in an attempt to grow crystals of the two fractions at even higher temperatures than has been accomplished so far. In addition, the effect of crystallization temperature on the

*Where B and A are the dimensions of the crystals parallel to [010] and [100], respectively.

habits of crystals of a third polyethylene fraction (Fraction III, Mn = 100500) is being pursued using the same solvent. Concurrently, experiments aimed at deducing the nature of the as-grown conformations of the crystals grown so far and exhibiting axial ratios in the range 1.7 to 6.0 are continuing. Scanning transmission electron microscopy and small area electron diffraction are the main tools being used in this connection. Among the difficulties encountered in characterizing the conformation of the crystals are the following features which have been encountered in the few species of crystals which have been explored so far: (a) variations in the tilt of the chain stems relative to the crystal surfaces both along and across the length of the crystals, and (b) apparent differences in stem tilts between crystals of different sizes grown at the same temperature and of the same polymer fraction. The latter effect, which has been encountered during the course of a comparison between crystals of Fraction I grown at 115 °C from unseeded preparations (large crystals) and "self-seeded" preparations (smaller crystals), is currently under study.

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Fracture Processes in Polymers
Subtask 3 of Task 12136

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The onset of failure under mechanical stress at the macroscopic level can be identified with either inhomogeneous deformation (necking) or crack growth. The former is treated in Subtask 4. Two aspects of crack growth that are particular to polymers are craze phenomena and time dependent fracture. Glassy polymers exhibit craze formation in the region preceding the crack tip. The failure of these materials is related to the growth of the craze region and its dependence on stress relaxation processes of the material. An adequate theoretical description of craze growth and its dependence on material properties s the aim of a recently initiated effort in the fracture of polymers. A successful model of the craze phenomena would provide an improved basis for life-time prediction.

A second activity in the fracture of polymers is concerned with elucidating the mechanisms by which elastomer additives improve the fracture toughness of epoxy matrix composites and the dependence of these mechanisms on time and temperature. Test methods are being developed that adequately measure the resistance of glass fiber reinforced composites to delamination. The dependence of the failure time of elastomer modified composites on temperature has been established. An Arrhenius-type temperature dependence is found that may be the basis for an accelerated test method.

Theoretical investigations of craze and crack growth. The investigation of the effect of relaxation of stresses within a craze at a crack tip on the rate of craze and crack growth is continuing. A manuscript entitled, "Relaxation of Stresses in Crazes at Crack Tips," has been completed and is undergoing editorial review.

For this investigation, the theory of cohesive stresses of Barenblatt [1] was applied to the craze growth problem, considering the uncrazed material to be elastic. In the Barenblatt theory, the magnitude σ of the cohesive (craze) stresses and the distance α (craze region) over which they act are given (for very small craze regions) by the equation

$$\int_0^{\alpha} \frac{\sigma(\xi,t)}{\sqrt{\xi}}\, d\xi = \sqrt{\pi/2}\, K_I \qquad (1)$$

where ξ is a coordinate within the craze and K_1 is the applied stress intensity factor. This is related to the applied stress σ_∞ and the crack length a by the equation

$$K_I = \sigma_\infty \sqrt{\pi a}\ \ f(a/w) \qquad (2)$$

where w is the specimen width and f(a/w) is a geometric factor determined by the specimen configuration.

The fundamental hypothesis of the Barenblatt theory is that the cohesive (craze) stresses cancel the stress singularity that would exist at the crack tip in their absence. In the present treatment, it is assumed that this singularity cancellation exists even for moving crazes. It is then clear from Eq. (1) that, for constant K_1, α must increase if σ decreases. A simple equation relating the rate of craze growth to rate of stress relaxation is obtained from differentiation of Eq. (1):

$$\frac{\sigma(\alpha,t)}{\sqrt{\alpha}}\cdot\frac{d\alpha}{dt} = \sqrt{\pi/2}\,\frac{dK_I}{dt} - \int_0^{\alpha} \frac{\partial\sigma}{\partial t}\frac{\phi u}{\sqrt{\xi}} \qquad (3)$$

where $\sigma(\alpha,t)$, is the stress at the trailing edge of the craze (i.e., the tip of the crack).

This integro-differential equation is the basic equation for this type of craze growth, called "relaxation controlled growth" by Williams and Marshall [2]. Its solution requires the knowledge of the rate of change of craze stress over the whole craze region. This latter problem can be formulated in terms of integral equations, but these are in general intractable. However, it can be said that the rate of relaxation of stress within the craze will in general be lower than the rate of the relaxation of stress for craze material in a normal (i.e., fixed length) stress relaxation experiment.

With some simplifying assumptions, Eq. (3) may be solved. The assumptions are:

(1) The craze initiation stress at the craze tip is a constant σ_0. This is equivalent to a stress criterion for craze initiation, which is considered reasonable for the triaxial stress state at the craze tip.

(2) At t = o, i.e., at the time of initial craze formation, the stress in the craze is independent of position within the craze, as in the Dugdale model [3]. This stress then relaxes with time, except at the craze tip, where growth occurs. This is called the "generalized Dugdale model."

(3) The stress intensity factor is a constant. Under these conditions, Eq. (3) may be solved to yield

$$\sqrt{\alpha}\,\sqrt{t} = \frac{1}{4}\sqrt{\frac{\pi}{2}}\,K_I \int_o^t \frac{dt}{\sqrt{t\sigma(\alpha,t)}} \qquad (4)$$

Assuming now that $\sigma(\alpha,t)$ varies exponentially with time as follows

$$\sigma(\alpha,t) = \frac{\sigma_o}{1 + (t/\tau)^m} \qquad (5)$$

where τ is in the nature of a relaxation time, and m is related to the slope of the compliance on a log-log plot, Eq. (4) may be integrated immediately to give

$$\alpha = \frac{\pi}{8}\frac{K_I^2}{\sigma_o^2}\left[1 + (t/\tau)^m \frac{1}{2m+1}\right]^2 \qquad (6)$$

For times long compared to τ, this equation gives satisfactory agreement with experimental results and gives the proper dependence on K_1. For short times, the relevant experiments are complicated by the presence of solvents. Clearly, the exact form of the solution will depend upon the time dependence taken for $\sigma(\alpha,t)$ in Eq. (4).

Present work is concerned with investigating more thoroughly the equations that determine the time behavior of the stress within the craze.

Experimental investigation of craze growth. Considering the importance to craze growth of the relaxation of stresses within the craze, a small experimental program to measure the creep function in craze material was begun. For this purpose, a sample of polycarbonate with large crazes grown in it was kindly provided by Dr. Roger Kambour of the G.E. research laboratory. This was then mounted on a jig, loaded to a stress of 800 psi (0.56 MN/m^2), and the thickness of the craze measured microscopically for a period of 24 hours. While the experiment suffered from lack of precision, preliminary results indicate that the function

$$\frac{J(t) - J(o)}{J(o)}$$

where J(o) is the instantaneous creep compliance and J(t) is the creep compliance at time t, is the same for the craze material as for the uncrazed substrate. This implies that the retardation times for creep are unchanged by the process of crazing, but this result will have to be confirmed in more careful experiments.

References:

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Influence of Matrix Properties on Delamination in Fiber-Reinforced Composites. The testing of fiber-reinforced composite panels in aerospace applications has revealed a problem with delamination. Composites are designed and utilized to take advantage of their high strength in the plane of the fibers. Unfortunately, it is not possible to totally eliminate out-of-plane loading. One of the problems that has been encountered in aerospace tests is impact damage during landing and takeoff. Such out-of-plane loading can lead to serious delamination because the organic matrix resins used to bind the fibers together in most composites are very brittle. This delamination can substantially reduce performance for both in-plane and out-of-plane loads. What makes this damage particularly troublesome is that it is often difficult to detect; once detected, it is difficult to assess how much the performance is affected; and if performance is seriously affected, delamination is often difficult to repair.

A number of studies have shown that when a matrix resin with improved fracture properties is used, the composite has significantly higher resistance to matrix cracking and other types of interlaminar fracture. Unfortunately, it is usually necessary to sacrifice other properties, such as modulus, to obtain improved fracture properties. Current work is investigating the use of rubber-modified epoxy resins. In these materials, the rubber is present as tiny particle-inclusions in a matrix of epoxy, and the two phase nature of these systems makes possible toughening mechanisms that cannot be achieved in single phase materials. As a result, these systems give very high fracture energies with a minimum sacrifice in other properties.

Fracture tests were conducted on neat resin specimens of modified and simple epoxies, and these tests show the large increase in fracture energy that can be obtained by rubber-modification. Both glass and carbon fiber reinforced composites were then fabricated with these resins and examined by propagating a crack in the matrix resin between the fiber layers. This test gives an interlaminar fracture energy which is one indication of the resistance of the composite to delamination. Such tests indicate that the interlaminar fracture energy of composites can be significantly increased by rubber-modification. Current work is aimed at developing a basic understanding of the mechanisms involved in composite failure and the factors which influence them. Such an understanding will provide guidelines for both improved composite designs and better materials.

Time-Dependent Fracture of Structural Adhesives. The high fracture energy of the rubber-modified epoxies has also made them the major constituent in most commercial structural adhesives. The mechanisms responsible for this high fracture energy are presently being studied with both bulk and adhesive bond specimens. A major result of this work is the demonstration that the toughening mechanisms are viscoelastic/plastic in nature, and thus, the fracture energy depends on the loading and temperature history of the sample. Experiments

have shown that the fracture behavior for bulk samples of this material subjected to simple types of loading and temperature histories can be described with simple empirical equations. For example, over a range of conditions, the time to failure, t_f, in constant cross-head speed tests can be related to a parameter, S_E, that measures the rate of increase in strain energy during loading by a simple power law with an Arrhenius temperature dependence

$$t_f = A(S_E)^{-n} e^{\Delta H/RT}$$

Although this empirical equation only applies to a limited set of conditions, the parameters A, n, and ΔH are quite useful for comparing the relative rate and temperature sensitivity for different formulations. Studies are now underway to examine more general histories and models for failure of these commercially important materials.

Instability and the Phenomena of Necking
Subtask 4 of Task 12136

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Failure of polymeric materials by neck formation and propagation depends on level of mechanical stress, temperature, as well as aspects of the molecular and physical structure. These relationships have been determined for polyethylene, a widely used thermoplastic. Analysis of these relationships have led to an empirical relation between the time required to reach a certain strain and the time at which a neck forms. For practical purposes, neck formation is identified as mechanical failure. Current work is aimed at developing models and experimental procedures to predict the instability point, that is, the time required for the material to reach the strain in question. A successful model and experimental procedures would provide a powerful method for predicting lifetime under conditions where neck formation is the mode of failure.

The Mechanical Behavior of Isotactic Polypropylene in Uniaxial Extension: Instability and the Phenomenon of Necking. A theory of stability for the deformation of viscoelastic bars which obey the BKZ theory [1] has been developed [2]. This theory is an extension of the one given by Ericksen [3] for elastic bars. For the appropriate strain potentials under certain loads in uniaxial creep and constant rate of extension, the bar will deform homogeneously for some time and then become unstable and neck. Ericksen's type of analysis has been applied to a viscoelastic situation in an effort to explain how time effects may enter into the onset of a discontinuity. While the theory does not predict a priori when the material will neck, it does give an explanation for the formation of the neck, which depends on the stretch history, and also shows how a material may, when fully necked, have a higher modulus than it had originally.

From constant rate of strain experiments in uniaxial extension, we have found that a slowly quenched sample of isotactic polypropylene can be described rather well by the BKZ theory. By this, we mean that the stresses in a constant rate of strain experiment calculated using the BKZ theory were in good agreement

with the experimental data. In all cases, the calculated values were lower than the observed values, but the maximum deviation was seven percent or less. This good agreement encouraged us to examine more closely the model proposed by Bernstein and Zapas concerned with the stability and cold drawing of viscoelastic bars.

A critical element in the application of the theory of Bernstein and Zapas is a knowledge of the single step stress relaxation behavior. For semicrystalline polymers such as isotactic polypropylene, single step stress relaxation data can be obtained only over a small region of strain. At strains above ten percent, the specimen necks during application of the step. However, the theory requires knowledge of such data over a much greater range of strain than is experimentally possible. Therefore, we have carried out a series of experiments involving a variety of different strain histories in uniaxial extension; these include single step stress relaxation, creep, constant rate of strain, and constant rate of loading. With the knowledge of the various strain histories, we have constructed one possible set of isochrones of stress vs strain by extrapolating our data into the regon of very high strains. From this set of curves and the instability theory, it is then possible to predict the point at which necking will occur for other strain histories.

We conclude that the Bernstein and Zapas instability theory may provide a reasonable description of the phenomenon of necking. This, we believe, may turn out to be a valuable procedure for predicting the incipient point of necking for even more complicated strain histories. The present work was undertaken as a first step for further investigation into understanding the phenomena of instabilities that may occur in other polymers.

References:

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Theory of the Instability and Failure of Viscoelastic Materials in Tension. In a tensile test of a bar or fiber formed from a transversely isotropic viscoelastic material, the initial motion in regions away from the clamps is a homogeneous uniaxial extension. If the applied tensile load is "tame" in the sense that it is given by a piecewise smooth function of time, then during the early stages of loading, the homogeneous extension of the specimen is also tame. It is often the case that at a time t_c, previous to the instant of fracture, the motion departs from a tame homogeneous extension. The critical time t_c is the "failure time" of the specimen, i.e., the time at which the motion first changes character; t_c precedes, often by a constant factor, the time at which neck-down is easily visible. The problem of calculating t_c for a given loading program has been treated within the framework of the general theory of non-linear simple materials with fading memory. For such materials, the instantaneous tensile modulus, i.e., the derivative of the immediate change in tensile stress with respect to a sudden change in tensile strain, depends upon the previous history of the strain. An explanation has been put forward for identifying t_c with the earliest time t_o at which the instantaneous tensile

modulus becomes zero. It has been shown that at a time at which the instantaneous modulus vanishes, one cannot arbitrarily assign the rate of change of tensile stress and have the motion remain in the class of tame homogeneous extensions.

Test Method Development
Subtask 5 of Task 12136

J. M. Crissman, D. L. Hunston, E. A. Kearsley, R. W. Penn, L. J. Zapas, G. M. Martin, J. L. Rushford

Test methods are developed for evaluating mechanical performance and durability of polymeric materials. A joint program with the Department of Transportation led to the development of an improved test for environmental stress cracking of plastics. The method has been presented to the ASTM and test conditions are being optimized in current work prior to submission for round robin testing. A cooperative effort with DOE addresses the need for test methods to evaluate the long-term performance of elastomeric seals used in geothermal energy production. A test protocol has been devised that circumvents the problem of carrying out measurements in extreme environments similar to those found in the use conditions.

A nondestructive measurement technique has been developed that permits dynamic mechanical testing and stress relaxation experiments as a function of temperature and time. The technique has been applied to the study of cure of composite materials and to the dependence of mechanical properties on aging time. The technique has application as a quality control method since an improperly prepared batch of thermosetting material can be easily detected.

Development of a New Test Method for Environmental Stress Crack Resistance. For thirty or more years, it has been recognized that ethylene-based plastics are susceptible to environmental stress cracking (ESC). This knowledge led to the rapid development of many test methods for evaluating environmental stress-crack resistance (ESCR), including those in most widespread use today. More recently, the use of ethylene-based plastics in the packaging industry has greatly expanded. One important area is that of hazardous materials transportation where because of increased energy constraints there is a demand for lighter weight shipping containers. The use of polyethylene in large shipping containers has been made possible in part by the development of new, more highly stress crack resistant polymer resins.

One result of this activity is that over the past several years there has been renewed interest in ESC and the development of new test methods which can, on a reasonable time scale, more adequately characterize ESCR. We have examined a number of test methods for ESCR and have developed one test which involves a bent strip geometry but differs from the current ASTM bent strip test in two ways: (1) all specimens are constrained in such a way as to maintain a constant geometry, and (2) the specimen is subjected to a constant applied load.

Tests are currently being carried out on three different polyethylenes having widely different ESCR. Two of the samples are linear polyethylenes having weight average molecular weights (M_w) of approximately 10^5 and 4.5×10^6, and the third is an ethylene-hexene copolymer having a M_w of about 2.1×10^5. The

test procedures being employed are intended to optimize the experimental conditions in order that data can be obtained in an acceptable time period for as wide a range of different polyethylenes as possible. Such procedures involve systematically changing the bend geometry, specimen thickness, magnitude of the applied stress, and temperature.

At the present time, the characterization of the two lower molecular weight samples is nearly complete. Work is continuing on characterization of the ultra high molecular weight material which requires very long times to collect data. It is anticipated that the data collection will be completed in about one year. Upon completion, a description of the test method as well as the appropriate statistical data will be submitted to ASTM Committee D-20.10 for their consideration.

Polymeric Sealants for Geothermal Energy. In a program to assist the Department of Energy to develop geothermal energy resources in the United States, we have been developing test methods for polymeric sealant materials to be used in the drilling of and producton of geothermal wells. Since there are many forms of seals used and down-hold environments vary considerably among the different well locations, it is not possible to specify reasonable requirements for geothermal sealants in general. The most interesting and energetically important wells are potentially those with ambient down-hold temperatures greater than 260 °C and with strongly corrosive, reducing (rather than oxidizing) atmospheres. The sealant materials should perform (frequently this means maintaining large elastic stresses for fixed deformations) under these demanding conditions for time periods ranging from hours for well-drilling sealants to months or years for production seals. Current technology for such seals is largely based on developments for the petroleum industry and is, consequently, adapted to lower temperatures and less corrosive conditions.

At present, various ad hoc lifetime tests are used by designers of geothermal equipment to test specific seals under conditions simulating the intended use. Such tests are very specialized and inconvenient. Failures of the seals are observed to occur either because the sealant hardens and eventually cracks or because the sealant softens and flows. The program on geothermal sealants in the Polymer Science and Standards Division aims at a more fundamental test which gets at the causes of this behavior so that the results can be used to design seals for whatever configuration or geothermal environment is needed. This is to be achieved by measuring the rates of formation and of breaking of bonds (cross-links or equivalent) using the method developed by Tobolsky, et al., to study oxidative degradation of rubber. In that method, two sets of measurements are required: (1) the stress relaxation of material aging while deformed and (2) the change in elastic modulus of material aging in an undeformed configuration. The latter data can be collected rather routinely, but stress relaxation is an inconvenient experiment, particularly under conditions corresponding to geothermal down-well atmospheres. Consequently, we have worked out the theory of a method to substitute permanent-set data for the stress relaxation data needed for the Tobolsky method. The theoretical work for this was completed previously.

Currently we have assembled apparatus in which we can age test samples in aqueous or dry atmospheres at pressures up to 3000 psi and at temperatures up to 300 °C. The apparatus is constructed of stainless steel. Pressures and atmospheres are limited to the gases available in commercial cylinders. Test specimens can be held in various constant states of strain during their aging. Apparatus has also been developed to facilitate mechanical testing of the specimens without reclamping them. Our computer controlled hydraulic test system has been programmed to conduct the necessary testing efficiently and to reduce the mechanical properties data.

Determination of Mechanical Properties for Characterization, Quality Control, and NDE of Polymers. Satisfactory performance of a polymeric material in a practical application is often directly related to the proper matching of the mechanical properties of the polymer to those required for the application over the range of temperatures and time scales involved. As a result, the measurement of mechanical properties can provide not only useful characterization data but also valuable quality control (QC) and NDE information. To obtain maximum benefit from mechanical property measurements, however, it is important that the behavior be determined over the widest possible range of temperatures and time scales (or frequencies). In this regard, a device has been constructed in cooperation with the Naval Research Laboratory to combine dynamic mechanical testing and stress relaxation experiments in a single instrument. This device provides data for low amplitude shear properties over an eight decade time scale range at temperatures from -200 °C to 400 °C. Samples can range from low viscosity fluids to highly cross-linked solids. The instrument is extremely versatile and has already been used to examine fiber reinforced composites, structural adhesives, high temperature plastics, elastomers, propellants, plastisols, and printing inks. To illustrate the use of this device, three particular examples will be briefly discussed.

The problem of quality control for elastomeric materials is a difficult one because many ingredients are used and a number of processing steps are involved. As part of the manufacturing procedure, it is customary to make a number of small samples (ASTM plates) for each batch to serve as material for QC testing. Our test device has been adapted so that a small portion of an ASTM plate can be utilized to provide a detailed characterization of shear properties. With this information, an improperly prepared batch can easily be detected, and since the mechanical properties are related to molecular structure and morphology, it is possible in a number of cases to determine what mistakes were made in the formulation.

The nondestructive nature of this measurement technique is particularly helpful when the device is used to follow changes that occur in a material such as during cure. Two examples of this type have been studied during the past year. The Navy is interested in the properties of certain polyvinyl chloride plastisols for their studies of the interactions between turbulent flow and compliant surfaces. It was found, however, that the properties of this material change as a function of time. Our studies were able to provide not only a detailed characterization of the basic properties of these materials but also an analysis of how the properties change as a function of aging time. A second example of this type involves the printing inks used by the Bureau of Engraving and Printing for making currency. These inks cure during the printing process, and thus, good performance can only be obtained when the flow properties

change in the required ways and at the proper rates during the cure. Studies are currently underway to characterize the properties of the inks as a function of cure so that better quality control techniques can be developed.

Nonlinear Behavior of Polymeric Materials
Subtask 6 of Task 12136

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Constitutive relations are needed that adequately describe the nonlinear relationships found between stress and strain in most polymeric materials. These constitutive relations give connections between the macroscopic observables stress, strain, stress relaxation, etc., and are the basis for accelerated test methodology and lifetime prediction.

Nonlinear Elastic Behavior of Rubber Materials. In work carried out during the past year, we investigated the behavior of the derivatives of the strain energy function with respect to the stretch invariants, $\partial W/\partial I_1$ and $\partial W/\partial I_2$, of peroxide cross-linked natural rubber at deformations lower than those reported previously. In the course of our work, we examined the effects of the degree of cross-linking and of aging on the derivatives of the strain energy function. Our experiments were carried out in torsion, where both the torque and normal force were measured, to determine the strain energy function derivatives at values of the stretch invariants of $I_1=I_2$. In addition, we carried out experiments in simple extension and simple compression at strains as low as $\varepsilon = \pm 1.0 \times 10^{-4}$. By assuming the validity of the Valanis-Landel form of the strain energy function, we were able to relate the behavior in torsion with that in extension and compression.

The salient results of our work in torsion are:

(1) In no instance did we find that $\partial W/\partial I_2$ becomes negative with decreasing strain; this is at variance with some results reported in the literature.

(2) The small strain torsional modulus, $G = 2(\partial W/\partial I_1 + \partial W/\partial I_2)$, is relatively unaffected by aging of the rubber, while the individual strain energy function derivatives, $\partial W/\partial I_1$ and $\partial W/\partial I_2$, change significantly.

(3) $\partial W/\partial I_2$ is relatively independent of cross-linking, while $\partial W/\partial I_1$ increases with increasing cross-linking.

(4) At low degrees of cross-linking, $\partial W/\partial I_1 \sim \partial W/\partial I_2$ for unaged samples. This result was unexpected.

The salient results of our work in extension and compression are:

(1) The apparent moduli in tension and compression at small strains are not equal.

(2) The values of the apparent modulus in tension and compression at very small strains does not become constant. Rather, as the deformation approaches zero, the modulus increases significantly.

Non-Linear Viscoelastic Behavior of Polymeric Materials. A new constitutive law which explains the differences between experimental results and currently existing theories for the nonlinear viscoelastic behavior of materials has been developed. The relationship between stress and strain for a shearing history can be written as:

$$\sigma(t) = - \int_0^\infty f_1 [\zeta^t(s), s] \, ds +$$

$$\int_0^\infty \int_0^\infty f_2 [\zeta^t(s_1), \zeta^t(s_2); s_1, s_2] \, ds_1 \, ds_2$$

where $\zeta^t(s) = \gamma(t) - \gamma(t-s)$ and $\gamma(t)$ is the shearing strain. For all $s, s_1, s_2 \geqq 0$:

$$f_1(0,s) = 0$$

$$f_2(b,0;s_1,s_2) = f_2(0,b;s_1,s_2) = 0$$

$$f_2(b,c;s_1,s_2) = f_2(c,b;s_2,s_1)$$

Experimental work has been commenced to determine the material memory functions f_1 and f_2. This work is focusing on the torsional responses of epoxy and poly(methyl methacrylate). Single and double step stress relaxation histories are required to determine these material functions. Results for other histories, such as constant rate of strain, will be compared with predictions from the theory.

Durability of Paper
Subtask 7 of Task 12136

J. C. Smith

Paper used to make currency should have a good balance between durability and cost, as the replacement of worn out currency is an expensive operation. Because of this, the Bureau of Engraving and Printing supports work at NBS to identify and characterize those aspects of the morphology of paper networks which affect durability. The research results are expected to contribute to the development of durable paper made from blended wood pulps instead of the more expensive cotton and linen pulps presently used.

To achieve these objectives, it is necessary to have an improved understanding of the relationship between the structure of paper, the morphology of the fibers, the processing conditions, and the mechanical and physical properties of the paper and its components. Over the past several years, studies at the

National Bureau of Standards on interfiber bondability and its relation to the force-elongation behavior of fiber networks have helped to provide some of this background information.

Tensile tests are performed on specimens cut from open-web handsheets of density $\sim 2.0\ g/m^2$. Experiments have shown that the resulting force-elongation curves fit an equation of the form

$$F = A[\exp(x/x_c) - 1]$$

where F is the force and x is the elongation. x_c is a scaling parameter having the dimensions of length, and A is a parameter that serves as a modulus of elasticity. The two parameters, A and x_c, are sensitive to the number of interfiber bonds per unit area in the specimens tested. Moreover, during a test A and x_c vary in value as the test proceeds, reflecting damage to the specimen and changes in the location of the bond breaks that occur. This possibility of characterizing the specimen at various stages of a test is expected to enable the calculation of a force level parameter representative of the average bond strength between fibers in a given test specimen.

The average force at which a specimen fails by progressive bond breaks depends upon the density of bonds and upon the average bond strength. During a test, the density of bonds diminishes, but it is hoped that the A and x_c parameters can be used to compensate partially for this effect. Experiments to test this idea are in progress.

Mechanical and Transport Properties of Polyethylene in Organic Solvents
Subtask 8 of Task 12136

J. C. Phillips, A. Peterlin

Polymer films are being used as liners for landfills and chemical waste holding ponds to control the movement of hazardous materials. In order to develop data that can be used to estimate the useful lifetime of such polymer liners, we have measured the transport of an organic acid through low density polyethylene (LDPE) and have measured the mechanical properties of LDPE in the presence of an organic vapor. The organic solvents simulate the action of the landfill leachates or hazardous waste.

The preliminary phase of this work invoved measurements of mass loss of acetic acid IHAc) in low density (LDPE) and high density bottles and sorption/desorption of acetic acid vapor in LDPE films. The mass loss measurements were performed at 40 °C, 60 °C, and 78 °C. At the highest temperature (t = 79 °C), mass loss for mixtures of HAc/H_2O were also done; the concentrations of HAc in volume percent were 100 percent, 75 percent, 50 percent, and 25 percent. From the mass loss-time data, the loss rate and timelag were determined for each density bottle. The former results, as a function of temperature, yield the activation energy of permeation, while the activation energy of diffusion was calculated from the latter results. The activation energy of permeation, E_p, was the same for each density bottle, and the activation energy of diffusion was uncertain due to errors in the time-lag determination. The loss rate data for the

solutions of HAc/H_2O was found empirically to be a function of the volume fraction, V, of HAc, i.e., $\log Q = K + V^{\alpha}$, where α is a constant and was set equal to 2.5.

The sorption/desorption data were obtained at 30 °C, 50 °C, and 70 °C at a vapor pressure of $p \sim 17$ mm Hg. The polyethylene film had a density of $\rho = 0.906$ g/cm^3 and a thickness of 10.16×10^{-3} cm. Diffusivity and solubility as a function of temperature indicated, respectively, that the activation energy of diffusion and the heat of solution were roughly constant for the range investigated. The diffusion process seems to be Fickian with differences in sorption and desorption behavior which suggest a concentration-dependent diffusion coefficient.

This preliminary study has shown that the density of PE is a very important factor in making a choice of a specific liner material. The temperature effect and the volume fraction of HAc in the leachate are also essential parameters that influence the mass loss and loss rate.

Mechanical properties of LDPE were analyzed by separating the total strain, ε, into elastic, ε_e, and plastic, $\varepsilon_{p\ell}$, components. These components were determined in air at $t \sim 23$ °C from recovery measurements for imposed strains of $\varepsilon_o = 9.0$ percent, 29 percent, and 54 percent by extrapolating $\varepsilon(t)$ data to $t = 0$. The extension times or the time the sample was held, t_h, varied from 10 minutes to 30 days. As a function of t_h, the elastic strain decreases while the plastic deformation increases. If recovery measurements are performed in the presence of an organic vapor (e.g., ethyl acetate), $\varepsilon_{p\ell}$ becomes greater than its air or vacuum value while ε_e tends to become less.

All recovery data could be roughly represented on a single master curve by plotting a reduced recovery $[\varepsilon(t) - \varepsilon_\infty]/(\varepsilon_o - \varepsilon_\infty)$ vs the logarithm of a reduced time of t/t_h. The plastic deformation at infinite time, ε_∞, is the permanent set of the material and also is a function of ε and t_h. The recovery data obtained in a vapor environment at pressure p could also be plotted on the master curve by assuming a reduced time of $(t/t_h)f(p)$ where $f(p)$ was found empirically to be $1/(1 + \alpha p)$ with α being a constant.

The results of changes of ε_e and $\varepsilon_{p\ell}$ with t_h correlate very well with changes of transport (diffusivity and solubility) with t_h and tend to emphasize the influence of the components of the total strain on the diffusion process.

MIGRATION AND THE DURABILITY OF POLYMERS IN USE
Task 12138

The most promising areas of growth in polymer markets are in construction, transportation, and electrical systems where long term durability is essential to competitive performance. Increased awareness of the problems of productivity and heightened competition has intensified this concern with durability in all polymer materials. Reliable test methods that reflect long term durability are needed for the selection of appropriate polymers for specific uses or to maximize industrial productivity by reducing overdesign of parts without inducing premature failure. Reliable methods for the prediction of the lifetime of polymers in service rely on three separate types of information: (1) knowledge of the rates and mechanisms by which the polymers degrade under the appropriate environmental conditions; (2) information concerning the rates of diffusion of protective additives; (Almost all commercial polymers are too sensitive to environmental attack to be used without protective additives. These low molecular weight substances such as antioxidants or stabilizers inhibit the degradation reaction and are dispersed throughoutte polymer to protect it. In use, these additives migrate through the polymer leaving the polymer markedly more vulnerable to failure.) (3) relationships connecting the changes in molecular properties to the commercially useful properties of the polymers. Work in this task is concerned with all three of these needs. Item (3) is addressed in both this task and in task 12135, Mechanical Durability of Polymers.

Technical work this year on degradation mechanisms and rates includes investigations of the hydrolysis of polyesters, a study of the mechanism of oxidation of polystyrene, the use of thermogravimetry to measure the rates and activation energies of the degradation of several polymers, and analysis of thermal methods of lifetime prediction.

For most commercial polymers, lifetime prediction methods must explicitly include the rates of additive diffusion along with the rates of the inhibited and uninhibited degradation reactions. The number of commercially usable polymer-additive combinations is too large to be considered eficiently on a case-by-case basis. The emphasis in this task is, therefore, on the development of general principles or models of diffusion that are applicable to the maximum number of commercially important systems. In addition, knowledge of the general principles which control diffusion through solid polymers is important to the design and evaluation of improved additive systems.

Polyolefins, which include psolyethylene and polypropylene, account for approximately half of the total polymer production. For this reason, the work in this task on models for diffusion is concerned exclusively with polyolefins which have their amorphous regions above their glass transition temperaturess in normal use conditions. We have developed a useful empirical correlation equation which relates the diffusion constants among a large number of polymer-additive pairs. Current work is now focused on the investigation of rapid and convenient methods for the measurement of diffusion rates by solvent extraction and inverses chromatography and on the accurate measurement of slow diffusion rates in solid polymers by microfluorimetry. These accurate measurements will provide improved data with which refined correlations can be constructed. These refined correlations should lead to theoretical descriptions of diffusion based on the molecular structure of the additives and the structure and morphology of the polymers.

Hydrolytic Degradation of Polyester Polyurethane Elastomers
Subtask 1 of Task 12138

D. W. Brown, R. E. Lowry, L. E. Smith

Polyester polyurethanes are versatile specialty polymers which are used to form tough and durable cast or molded elastomeric parts such as oil seals, gaskets, and electrical connectors. They are frequently used in critical and demanding service where the lifetime and performance of major systems depend on their durability. Some examples include aircraft engines, ship propulsion assemblies, submarine oxygen generators, and nuclear reactor control rod actuators. In order to provide reliable lifetime prediction methods for such applications, we have measured the rates of chain scission of unstabilized polyester polyurethanes. Activation energies for the degradation were measured to enable the use of accelerated test methods. We then devised a rapid and convenient measurement method which uses the acid contents of the polymers to predict degradation rates in service.

During this year we have measured the rates of the inhibited reaction to evaluate the effect of stabilizers on the expected lifetime and have produced a test method which gives results that correlate well with field experience.

We have recently described the hydrolytic breakdown of carbodiimide-stabilized polyester polyurethanes [1]. Polyester degradation ordinarily occurs by an acid catalyzed hydrolysis of the ester linkages. Carbodiimide stabilizes the polymer by reacting with acid, thus preventing catalysis. We have shown that uncatalyzed hydrolysis of ester also occurs. This reaction produces acid at a slow rate which reacts with the carbodiimide, eventually consuming it. Thereafter, acid catalysis again becomes important. Consequently, there were three rate constants to consider: k_0 for uncatalyzed hydrolysis, k for acid catalyzed hydrolysis, and k' for reaction of acid with carbodiimide. These were evaluated separately from the slow disappearance of carbodiimide, polymer hydrolysis without stabilizers, and reaction of polyester acid and carbodiimide in a dry polyester polyurethane, respectively. Differential equations for the combined reactions were then numerically integrated to generate curves that show the time dependence of the acid concentration, [A], the carbodiimide concentration, [M], and the change in the reciprocal of the number average molecular weight, $\Delta(M_n^{-1})$. This last is equal to the number of chain scissions. The figure shows one set of curves and the corresponding experimental data for stabilized and unstabilized polymers. The increase in service life due to the presence of carbodiimide is approximately equal to $([M_0]-[A_0])/k_0$, where the subscripts indicate use of concentrations measured after incorporation of the carbodiimide in the polymer. Values of k_0 depend on temperature but are the same for polycaprolactone and polybutylene adipate based polyurethanes of laboratory and commercial origin. Consequently, the k_0 should be generally useful in estimating lifetimes of stabilized polyurethanes.

Two aspects of the hydrolysis are still being studied. One is the dependence of k_0 on the urethane content of the polymer, since k_0 of polyester diols is three- to ten-fold less than k_0 of the corresponding polyurethanes. The other concerns the position of the ester-acid equilibrium in polyester diols and polyurethanes. This equilibrium would define an optimum environmental condition where no further hydrolysis would occur. This has important implications for archival uses of polyesters for information storage and retrieval.

Reference:

[1] D. W. Brown, R. E. Lowry, and L. E. Smith, The Hydrolytic Degradation of Polyester Polyurethanes Containing Carbodiimides, submitted to Macromolecules.

Long Term Aging Studies With Poly(Ethylene Terephthalate)

Subtask 2 of Task 12138

D. W. Brown, R. E. Lowry, L. E. Smith

Polyesters are the base material of a number of information storage and retrieval systems, such as photographic film, magnetic video and audio recording tape, and electrographic record systems. These storage media are replacing paper books and records even in archival storage because of their much higher information densities. In a project sponsored by the National Archives, we are investigating methods for estimating the useful lifetimes of polyesters and attempting to define optimum storage conditions for these materials.

Hydrolysis of the ester linkage is the most important cause of degradation. Thus, the general behavior of the polyester polyurethanes is expected to occur, with complications caused by the higher glass temperature (~ 70 °C), the presence of crystallinity, and the extreme orientation needed to make a strong film.

Experiments that have been set up include agings in air at 0, 25, 50, and 100 percent relative humidity (RH) at temperatures of 35, 55, and 85 °C. One set of samples at 100 percent relative humidity is in sealed tubes under nitrogen. Amorphous, unoriented samples are also being aged. Samples include a variety of commercial record-keeping films as well as samples of the NBS SRM 1470, a polyester film. Measurements being made on the samples include tensile tests, acid analysis by titration, molecular weight measurements by gel permeation chromatography, and examination by differenital scanning calorimetry.

To date, we have found that 90 days aging of SRM 1470 at 100 percent RH at 85 °C causes ~ 90 percent loss in tensile strength and a reduction in the number average molecular weight from 14500 to 6300. A sample aged at 100 percent RH at 55 °C for 90 days lost negligible tensile strength, and its molecular weight was 12600. Calorimeter scans showed no significant effects on the main melting peak (~ 255 °C) compared with the original material, but small peaks were introduced near the aging temperature. Very severe degradation resulting in weak, brittle samples occurred at 100 percent RH in 13 days at 115 °C and in 39 days at 100 °C, molecular weights being ~ 2800 and ~ 3100, respectively. With these samples, the melting peak was much broadened, with maxima occurring at 243 and 249 °C, respectively. Peak areas were increased about 20 percent.

It is planned to take advantage of the autocatalytic effect by preaging samples at 85 °C, 100 percent RH and then aging the samples under milder conditions, where the high acid content will result in more rapid changes.

Oxidation of Polystyrene
Subtask 3 of Task 12138

B. Dickens

Polystyrene is a high volume commodity polymer subject to oxidation in use. The mechanism of oxidation under normal use conditions is not known with certainty. Studies carried out in collaboration with Dr. Jean Marchal of the CNRS, Strasbourg, have used γ-ray initiated oxidation of polystyrene to simulate the low temperature oxidation process encountered under normal use but with control over the rate of radical initiation.

Oxidation studies have been carried out on polystyrene in chlorinated hydrocarbon solutions. Product analysis coupled with measurements of molecular weight changes have led to a number of conclusions. Under these circumstances we conclude that: the attacking species are Cl radicals, attack is random along the chain, intramolecular propagation of the oxidation chain occurs by hydrogen abstraction by peroxyl radicals, on the average there is one such propagation step in $CHCl_3$ and six in CCl_4, higher molecular weights are attacked less per monomer unit than lower molecular weights, and alkoxyl radicals are formed and undergo β-scission to break the polymer backbone and produce small molecules. In the solid these small molecules would plasticize the material. An oxidation mechanism to account for these facts has been devised.

Variable Heating Rate Thermogravimetry
Subtask 4 of Task 12138

J. H. Flynn

The concept of measuring the degradation of a polymeric material under conditions designed to accelerate its rate and extrapolating the rates to milder conditions so as to predict the lifetime of the material has great appeal. The practical uses and commercial importance of reasonably accurate lifetime prediction methods are obvious. The methods of thermal analysis are often used in lifetime prediction procedures. They offer practical advantages such as accessibility of apparatus, simplicity of application, and rapid accumulation of data. Thermogravimetry is the method of thermal analysis most often used for this purpose because the kinetics of volatilization are often closely coupled to the kinetics of degradation in the condensed phase.

Unfortunately, the application of the Arrhenius equation to polymer degradation processes for the purpose of predicting aging at service conditions is complicated by the complex kinetics of these reactions. Such heterogeneous systems are often composed of at least several "elementary processes," each with its own set of Arrhenius parameters. A change in activation energy will result from a change in the rate-limiting step of the degradation mechanism. If this occurs in the unmonitored kinetic gap between the lowest experimental temperature and the service temperature, then the lifetime prediction is invalid.

In our variable heating rate method, kinetic data are compared over a thousand-fold range of heating rates--from six degrees/minute to nine degrees/day. As a result, activation energies are obtained from five to 95 percent conversion for over a hundred degree temperature range and down to much lower temperatures

than those of the conventional methods of thermal analysis. From isoconversional diagnostic plots of logarithm heating rate vs reciprocal absolute temperature, activation energies are calculated for each fraction of conversion. The wide range of temperatures which these measurements cover gives one the precision necessary to determine the activation energies from the slope between each successive pair of points on each isoconversional. A grid may be set up from these values in which activation energies (E) are displayed as a function of conversion and temperature. This new technique has been applied to the degradation kinetics of polystyrene, poly(methylmethacrylate), and polyurethanes in inert atmosphere and in air. In the case of poly(methylmethacrylate) in nitrogen, for example, activation energy grids demonstrate that E increases with increasing temperature at constant conversion, but E appears to be nearly independent of conversion at constant temperature.

Analysis of the Kinetics of Thermogravimetry
Subtask 5 of Task 12138

J. H. Flynn

The kinetic analysis of the thermogravimetry of polymers requires the comparison of data from experiments performed at differing temperature programs. These data reflect divergent physical properties and chemical compositions among the specimens resulting from their diverse thermal histories. The effect of thermal history on the kinetics of weight-loss processes is a serious problem. However, it is not usually dealt with during the modeling of the kinetics of these processes. A reason for this is that often the effect can be exposed only through the comparison of calculated parameters from two separate series of kinetic measurements on identical specimens of polymers. Otherwise, contradictions in values of kinetic parameters from different techniques and investigations may either be overlooked or falsely ascribed to other causes such as experimental error, differences in initial chemical or physical properties of the samples, differences in experimental conditions, etc.

The critical test for thermal history dependence is differing rates of weight loss from two experiments at the same temperature and conversion, i.e., at a point of concurrence. The conventional methods for the determination of Arrhenius parameters involve either the comparison of two or more isothermal experiments at differing temperatures or the comparison of two or more constant heating rate experiments at differing heating rates. Neither of these cases realize a point of concurrence between two experiments.

Two experimental techniques and methods of data analysis have been developed to detect thermal history dependence of Arrhenius parameters. In the first method, logarithms of the times to reach various fractions of conversion for several isothermal experiments are plotted against the reciprocal absolute temperatures at which the same fractions of conversion were reached in a single experiment at constant heating rate. The slopes of the isothermals are given by:

$$\text{isothermal slope} \sim -1.05\ ER^{-1}$$

and the isoconversional distance between two isothermals, T_a and T_b, is

$$\text{isothermal distance} = ER^{-1}(T_b^{-1} - T_a^{-1}).$$

If thermal history effects are present, then the activation energy (E) calculated from the slopes will differ significantly from E calculated from the isothermal distances.

Similar sets of equations have been developed in the second case in which a single isothermal experiment is compared with several experiments at various constant heating rates. For this case, E's obtained from the isothermal distance between two isothermokinetics are compared with those obtained from the slopes of the isothermokinetic lines. As before, any difference between E calculated from the slopes and E calculated from the distances will indicate thermal history dependence. Also, in either case, any deviation of E from constant value can be observed visually from a distortion of the uniform distances or from changes in slope of the grids.

Activation energies have been determined with great precision for the degradation of polystyrene in vacuum from both the factor jump and constant heating rate techniques. The E values from the two methods show a significant difference of 11.1 kJ/mol. This difference has been interpreted as due to a bias from a constant increment caused by different thermal histories for each rate of heating.

Thermogravimetric Studies of Polymer Degradation
Subtask 6 of Task 12138

B. Dickens

Because of its ease of application, thermogravimetry is widely used to study polymers. However, this ease of application also induces a significant amount of misapplication. The appropriate kinetic treatments for thermogravimetric data have been examined and reviewed in joint work with J. H. Flynn. The parameter most readily determined is the activation energy, which can then be used to shed some light on the degradation mechanism.

In recent degradation studies, the following activation energies were found: 65.4 ± 0.5 kcal/mol for both linear and branched polyethylene (LPE and BPE) degrading in vacuum, 64.8 ± 0.3 kcal/mol for LPE and 64.4 ± 0.2 kcal/mol for BPE in slowly flowing N_2 at 8.0 mm Hg, and 6.26 ± 0.5 kcal/mol for LPE and 61.2 ± 0.6 kcal/mol for BPE in N_2 flowing at 1.0 to 4.0 mm/s at 800 mm Hg. The overall activation energy in vacuum has been related to a degradation mechanism to show that the slow chain-breaking step is one of β-scission following hydrogen abstraction. The procedure provides an estimate of 33 kcal/mol for the activation energy of β-scission for secondary alkyl radicals. For degradation by random scission of C-C backbone bonds in the initial stage, the overall activation energy is estimated to be 70.6 kcal/mol. The lower activation energies in the presence of an external pressure have been shown to be due to the evaporation of molecules formed in scissions but not volatilized immediately after their formation. This adds a latent heat term (10 ± 20 kcal/mol) to the apparent activation energy.

Similar quantities have been determined for isotactic polypropylene: 61.5 ± 0.8 kcal/mol in vacuum, 55.9 ± 0.3 kcal/mol in N_2 at 5.0 mm Hg, and 55.1 ± 0.2 kcal/mol in N_2 flowing at 1.0 to 4.0 mm/s at 800 mm Hg. The decompo-

sition of the activation energy into its components for degradation in vacuum provides an estimate of 29.6 kcal/mol for the β-scission of tertiary alkyl radicals. As was the case for PE, the lower activation energy for degradation under external pressure has been shown to be due to the latent heat contributions of molecules which do not evaporate as soon as they are formed. For the initial stage of degradation in vacuum, an activation energy of 71 kcal/mol is proposed.

Measurement of Antioxidant Diffusion by Microfluorimetry
Subtask 7 of Task 12138

S. L. Wunder, F. W. Wang, R. A. Velapoldi[1]

[1]Center for Analytical Chemistry.

Measurement of the concentration profiles of a diffusion substance is an accurate method for determining relatively small diffusion constants in the solid state. In addition, the effect of solvent on the diffusion rate can be measured on the same system which will allow direct comparison with diffusion rates measured by rapid and convenient solvent extraction methods.

The migration of antioxidants from polymer films is being studied by both extraction experiments and solid state diffusion experiments. In an extraction experiment, a plan sheet of polymer with uniform concentration of an antioxidant is immersed in a limited amount of well-stirred solvent. Then, the amount of the antioxidant extracted by the solvent is determined at various times by fluorimetry. The extraction of N,N'-diphenyl-p-phenylendiamine (DPPD) by heptane at 22.0 °C from low density polyethylene films has been measured. An analytical working curve relating DPPD concentration to fluorescence intensity was linear in DPPD concentration below 4.0 ppm. A preliminary report of the results has been prepared.

The diffusion of the antioxidant N,N'-β-dinaphthyl-p-phenylene-diamine (DNPD) in branched polyethylene (PE) SRM 1476 is being studied using microfluorimetry. After fusion of two plugs, one neat PE and the other doped with antioxidant, measurement of the antioxidant fluorescence as a function of distance from the fused boundary yields the diffusion coefficient of the antioxidant. This solid state diffusion technique eliminates the problem of the swelling effects in extraction experiments. Preliminary work has been performed to optimize the experimental conditions and techniques for the diffusion measurements. These will be obtained for DNPD in PE as a function of temperature.

Migration of Oligomers and Antioxidants From Polyolefins
Subtask 8 of Task 12138

S. S. Chang, W. J. Pummer, J. R. Maurey, L. E. Smith

Under the sponsorship of the Food and Drug Administration, this project aims at the development of general principles and models of diffusion that can be used to simplify the regulations governing polymers in food contact use and thus ease the burden of Federal regulations necessary for public health and safety. This work is also directly applicable to the design and interpretation of extraction methods for diffusion measurement and the models developed will be applicable to the

problem of lifetime prediction as well. In this year, copolymers of ethylene and vinyl acetate with vinyl acetate contents of five and 13 percent have been added to the list of polyolefins studied. Several solvents have also been added to the list of solvents used.

Thus, the experimental variables include (1) polymers--linear polyethylene, branched polyethylene, isotactic polypropylene, and copolymers of ethylene and vinyl acetate; (2) migrants--n-$C_{18}H_{38}$, n-$C_{32}H_{66}$, and BHT; (3) solvents--corn oil, tributyrin, trioctanoin, ethanol, ethanol-water mixtures, water, n-heptane, n-octanol, synthetic triglyceride mixture HB307, and n-octadecane; and (4) temperature--30, 40, and 60 °C. Furthermore, the initial concentrations of the migrants in the polymers and the thickness of the sample plaques have also been varied. Besides the kinetic studies, equilibrium properties such as solubilities and partition coefficients have also been studied. The migrants used are labeled with radioactive ^{14}C to yield a detectibility of 10^{-10} g if needed. The extraction experiments generally require a few weeks to a few months to complete; however, some experiments may reach completion in less than a day, while some may last longer than a year. The diffusion coefficients observed vary from 10^{-6} - 10^{-15} cm^2s^{-1}. Some of the experiments indicate an ideal Fickian behavior, especially for preswollen polymers or for non-swelling solvents. In most solvents, the diffusion coefficient may increase from an initial value and then level off at a higher value due mainly to swelling effects.

If all other parameters are held constant, then the ranking of importance for the parameters on the diffusion coefficient of migrants from polyolefins is as follows: solvent, temperature, additive type, polymer type, additive concentration. The first three parameters are far more important than the remaining two.

The nature of the effect of the first three variables is also rather different from those of the latter. The effect from the most influential group of variables (solvent, temperature, and migrant) is generally much less pronounced for cases producing high diffusion coefficients, e.g., 10^{-6} cm^2s^{-1}, than for low diffusion coefficients. For instance, the effect of replacing a lower MW oligomeric migrant, n-$C_{18}H_{38}$, by a higher MW migrant, n-$C_{32}H_{66}$, under various conditions is shown in figure 2 as an illustration for this type of behavior. The effect is less than a factor of five at diffusion coefficients of 10^{-7} to $10^{-6}cm^2s^{-1}$, while the ratio is near 1,000 at diffusion coefficients of 10^{-10} to $10^{-9}cm^2s^{-1}$. Similar behavior is observed by changing solvents or temperature.

However, in the case of changing polymers, the effect seems to be more or less a constant shift in the ratio of the diffusion coefficients covering a wide range of diffusion coefficients. This behavior is illustrated in figure 3 where the diffusion coefficients of migrants from low crystallinity, branched polyethylene are compared against those from highly crystalline, linear polyethylene (as well as polypropylene) in various combinations of other parameters. The average ratio of the coefficients for changing the base polymer only is about six through the range of diffusion coefficients from 10^{-14} to $10^{-6}cm^2s^{-1}$.

In contrast to the great accelerating action of n-heptane over that of corn oil in extracting small molecules from polymers (NBSIR 81-2263), the diffusion coefficients of these small molecules into liquidus tributyrin, trioctanoin,

and synthetic triglyceride HB307 are nearly identical to that into corn oil within a factor of 1.5. Therefore, either tributyrin, trioctanoin, or HB307 can be used to simulate the extractive action of corn oil in a great variety of conditions involving different additives, polyolefins, and temperatures. However, normal analytical techniques (other than radiolabeling) are difficult with the triglycerides. Diffusion coefficients into ethanol are equal or slightly greater than that into triglycerides under similar combinations of test conditions and chemical analysis in ethanol is generally much easier than in the triglycerides. The slightly enhanced extraction behavior makes ethanol a slightly accelerating solvent which yields an upper bound for migration.

Results for n-octanol and 95 percent ethanol yield supplemental information for using ethanol as a simulating solvent. Octanol also behaves as an accelerating solvent, although its accelerating action is far below that of n-octadecane and n-heptane. Diffusion coefficients of these small molecules are about the same into pure ethanol and into 95 percent ethanol. However, the lower solubility and partition coefficients of some of the migrants in 95 percent ethanol yield a lower limit of migration of these molecules at equilibrium than that in anhydrous ethanol.

Measurements of Diffusion in Polymers by Inverse Gas Chromatography
Subtask 9 of Task 12138

G. A. Senich

Diffusivities of volatile compounds or probes in polymers have been obtained from non-equilibrium inverse gas chromatography (IGC) experiments conducted at rapid carrier gas flow rates. The experiment is similar to conventional gas chromatography (GC) except that the polymer under study replaces the usual low molecular weight stationary phase. The quantity of interest is the measured peak broadening that occurs during flow through the column. Peak spreading arises from the multiplicity of differing gas paths through the column, diffusion in the gas phase along the flow direction, and resistance to mass transfer in both the gas and polymer phases, among other factors, and is commonly related to the probe-polymer diffusion coefficient by the well-known van Deemter equation in GC. However, this relation neglects variations in the local carrier gas flow velocity and some additional diffusive processes in the gas phase. These factors have been shown to exert a significant influence on the magnitude of the diffusivity found by IGC studies.

Another important parameter is the diffusion path length in the polymer phase. Two extremes in polymer geometry are possible within the column, a thin, uniformly distributed covering over the entire surface of the spherical column packing or annulus-like regions collected at the contact points between spheres, each with a different diffusion path length. These two extremes in the physical distribution of the polymer phase can lead to polymer-probe diffusivities differing by factors of up to ten thousand. The variability of the polymer film throughout the column makes an accurate determination of the absolute probe-polymer diffusivity unlikely. Experiments on the rate of diffusion of one probe relative to another in the same polymer column are currently in progress. The resulting relative diffusivities may then be placed on an absolute scale by calibrating the column with a probe whose diffusion coefficient in the polymer has been determined by an independent method.

The extent of migration of a sufficiently volatile material from a polymer into a contacting substance (typically a solvent) can be estimated from data readily obtained by IGC studies. The specific retnetion volume obtained experimentally at slow carrier gas flow rates, which characterizes the thermodynamic interactions between the probe and polymer, is used to determine the polymer-migrant interaction parameter. When combined with a value of the solubility of the migrant in the solvent, a calculation of the equilibrium partition coefficient is possible. The latter is a direct measure of the fraction of the additive which can be expected to migrate from the polymer to the contacting medium. If the time over which migration can occur is short, an equilibrium prediction may greatly exaggerate the degree of migration expected. A value for the diffusion coefficient of the migrant in the polymer may then be obtained from IGC experiments and employed to estimate the degree of migration which will occur over the given time period. A recent publication [1] outlines in greater detail a procedure for determining the extent of migration at both equilibrium and short times from data derived by IGC studies.

Reference:

[1] G. A. Senich, Chem. Tech. 11, 360 (1981).

Measurement of Translational Diffusion of Polymers by Fluorescence Photobleaching Recovery Technique
Subtask 10 of Task 12138

F. W. Wang, W. H. Grant

The diffusion coefficient of chain molecules is a dynamical parameter which should provide a test of both scaling [1] and reptation [2] concepts proposed by de Gennes. Recently, Hervet and co-workers [3] used the forced Rayleigh scattering technique to measure the diffusion coefficient (D) of polystyrene chains in benzene. They found that in the semidilute regime where the chains overlap, D decreases with polymer concentration, c, as $c^{1.7 \pm 0.1}$, in agreement with scaling law predictions. However, they pointed out that more experiments are necessary to check the molecular weight dependence of the diffusion coefficient.

In collaboration with Prof. En-Shinn Wu of the University of Maryland (Baltimore County), we have initiated a project to measure by fluorescence photobleaching recovery (FPR) technique the diffusion of chain molecules in the semidilute regime. In the FPR technique, one uses high intensity illumination to deplete the observed volume element of chromophore-labeled chain molecules by photobleaching. After the bleaching pulse, the diffusion of unbleached chromophore-labeled chain molecules into the volume element is observed with low intensity illumination. From the time constant for the recovery of the original fluorescence intensity, the diffusion coefficient can be obtained. The FPR technique can be used to measure diffusion coefficients in the range $10^{-11} cm^2/s$ to $10^{-6} cm^2/s$ [4].

We have developed a procedure to synthesize polymers labeled with photobleachable chromophores and have determined the fluorescence properties of one of these polymers. The diffusion coefficients of this and other similarly prepared polymers will be measured by using the FPR technique at the University of Maryland by Prof. Wu to check the molecular weight dependence of the diffusion coefficient in the semidilute regime.

References:

[1] P. G. de Gennes, Macromolecules, 9, 594 (1976).
[2] P. G. de Gennes, J. Chem. Phys. 55, 572 (1971).
[3] H. Hervet, L. Léyer, and F. Rondelez, Phys. Rev. Lett. 42, 1681 (1979).
[4] D. E. Koppel, D. Axelrod, J. Schlessinger, E. L. Elson, and W. W. Webb, Biophys. J. 16, 1315 (1976).

Assessment of Transport Mechanisms For Radon In and Through Building Materials

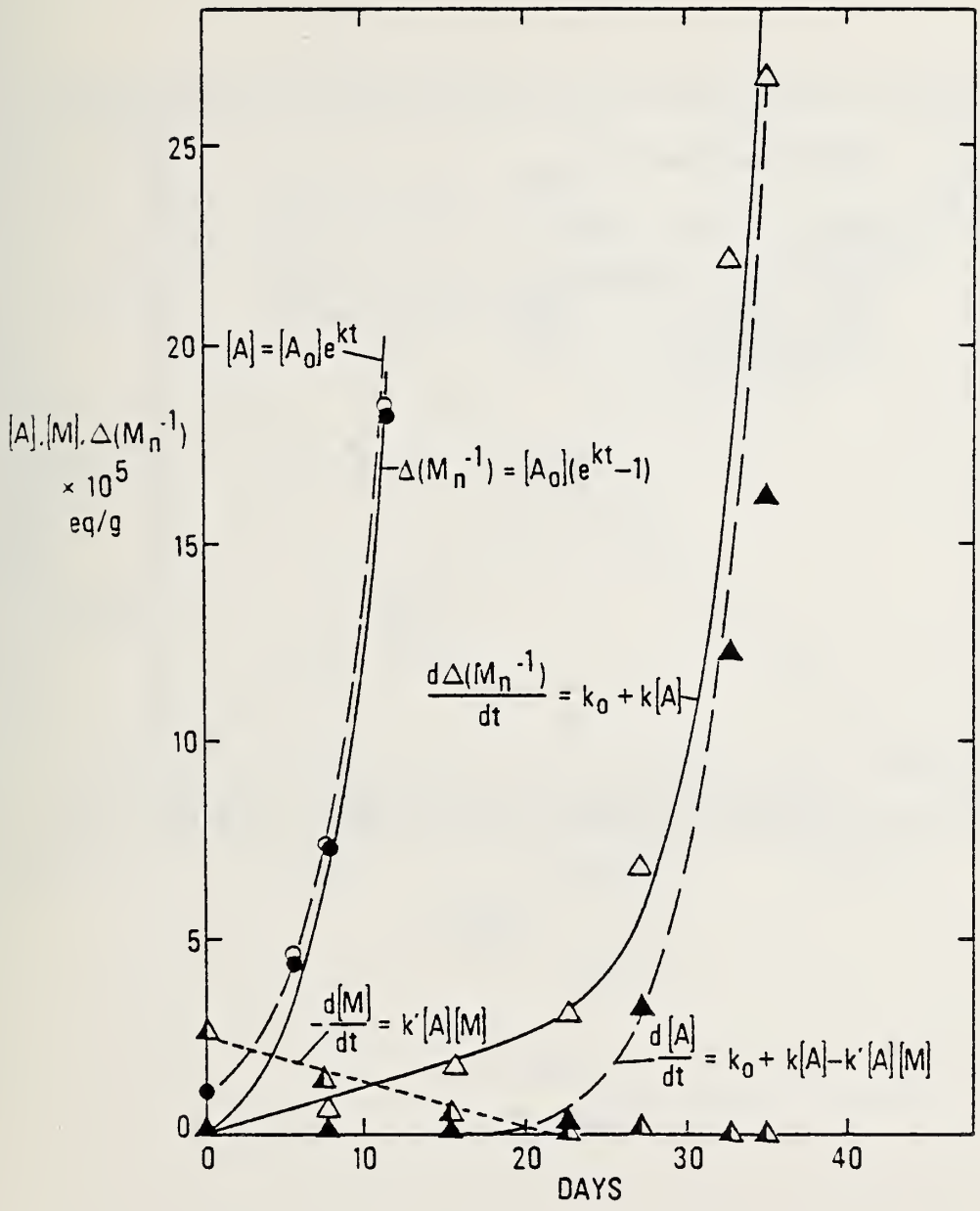
Subtask 11 of Task 12138

R. J. Rubin

Accumulation of radioactive radon gas in buildings poses a health hazard. High levels of radon are encountered in certain geological areas where the naturally occurring amounts of radium-226 are high. Certain building materials, such as concrete, building blocks, and gypsum board, may also produce higher than average amounts of radon if one of the components of the building material contains high trace concentrations of radium-226. Under an interagency agreement with the EPA, NBS has very recently undertaken the task of studying radon transport in building materials. The study involves a cooperative effort between three NBS Centers: Radiation Research, Building Technology, and Materials Science. The initial phase of this project, to critically assess the current state of knowledge of radon transport through or emanation from building materials, has been completed. Because of our expertise in diffusion and transport models, the Polymer Science and Standards Division was asked to assess current mechanisms,and models and apply them to some selected cases.

Models of the movement of radon through and from porous building materials such as concrete are based on the assumption that the transport of radon through the air-filled pore system of a porous material occurs in response to two driving forces: (1) diffusive transport of radon in response to a difference in radon concentration, where the transport coefficient is the diffusion coefficient of radon in the air-filled pore system, and (2) convective transport of an air-radon mixture in response to an air pressure difference, where the transport coefficient is the permeability coefficient of air in the pore system. Among the questions and transport cases which have been treated are: (1) What are the relative contributions of concentration differences and pressure differences to the steady-state transport of radon in concrete? From literature values of the diffusion coefficient of radon in concrete, the porosity of concrete, and the permeability coefficient of air in concrete, we have found that a pressure difference of 25 mm Hg across 10 cm of concrete significantly enhances the flux of radon through a surface. (2) Estimates are obtained of the times required to establish steady-state behavior in both the case of diffusive transport and convective transport. In general, the time required for establishing steady-state convective transport is a few hours when the time required for establishing steady-state diffusive transport is a few days. Thus, it appears that short term variations in radon concentration (of the order of one day or less) are "averaged out." (3) The factor by which the steady-state radon flux from bare soil is reduced when a concrete slab is interposed is calculated.

These and other examples are incorporated in the report, "Review and Assessment of Radon Transport Through and From Building Materials," which has been reviewed favorably by a number of experts in the field and will be published as an NBS Technical Note. Among the recommendations which have been made on the basis of our study for this report are: (1) The time-dependent transport equations for transport of radon in a porous medium which include both diffusive and convective terms should be verified or validated. (2) Measurements of the diffusion coefficient of radon and the permeability coefficient of air should be made on the same concrete specimens. It is only through such combined measurements that the relative magnitude or importance of the two kinds of transport can be determined with certainty. (3) An experiment has been proposed to determine the diffusion coefficient of radon in concrete from measurements of the build-up of radon concentration with time when a specimen of well-defined shape is placed in a radon chamber. The model case of a cylinder with exposed ends and coated side has been analyzed.


25
20
15
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5
0
0
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40
DAYS
[A].[M].Δ(Mn-1) × 10^5 eq/g
[A] = [A0]e^kt
Δ(Mn-1) = [A0](e^kt−1)
dΔ(Mn-1)/dt = k0 + k[A]
−d[M]/dt = k'[A][M]
d[A]/dt = k0 + k[A]−k'[A][M]

Figure 1

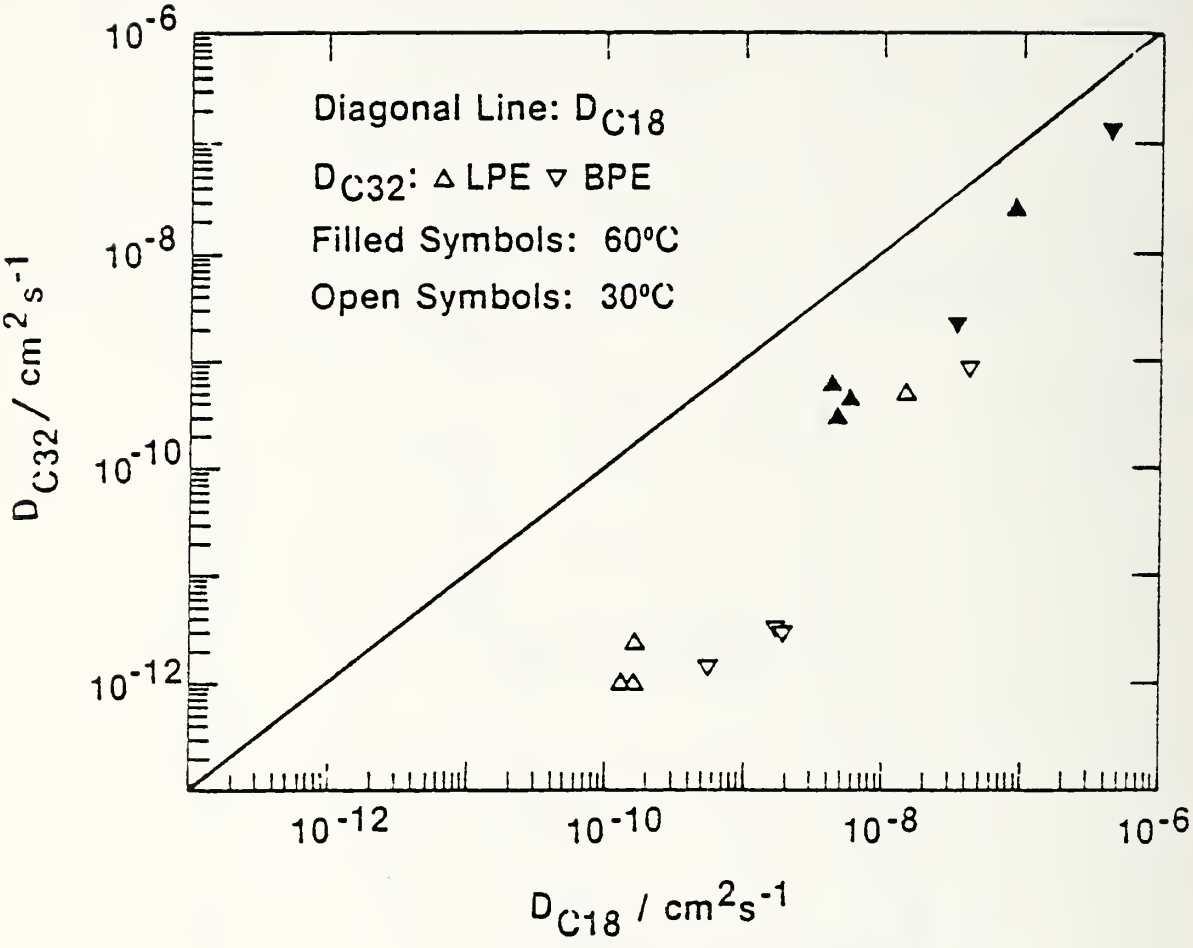
Diagonal Line: D_{C18}
D_{C32}: △ LPE ▽ BPE
Filled Symbols: 60°C
Open Symbols: 30°C
10^{-6}
10^{-8}
10^{-10}
10^{-12}
D_{C32} / $cm^2 s^{-1}$
10^{-12}
10^{-10}
10^{-8}
10^{-6}
D_{C18} / $cm^2 s^{-1}$

Figure 2

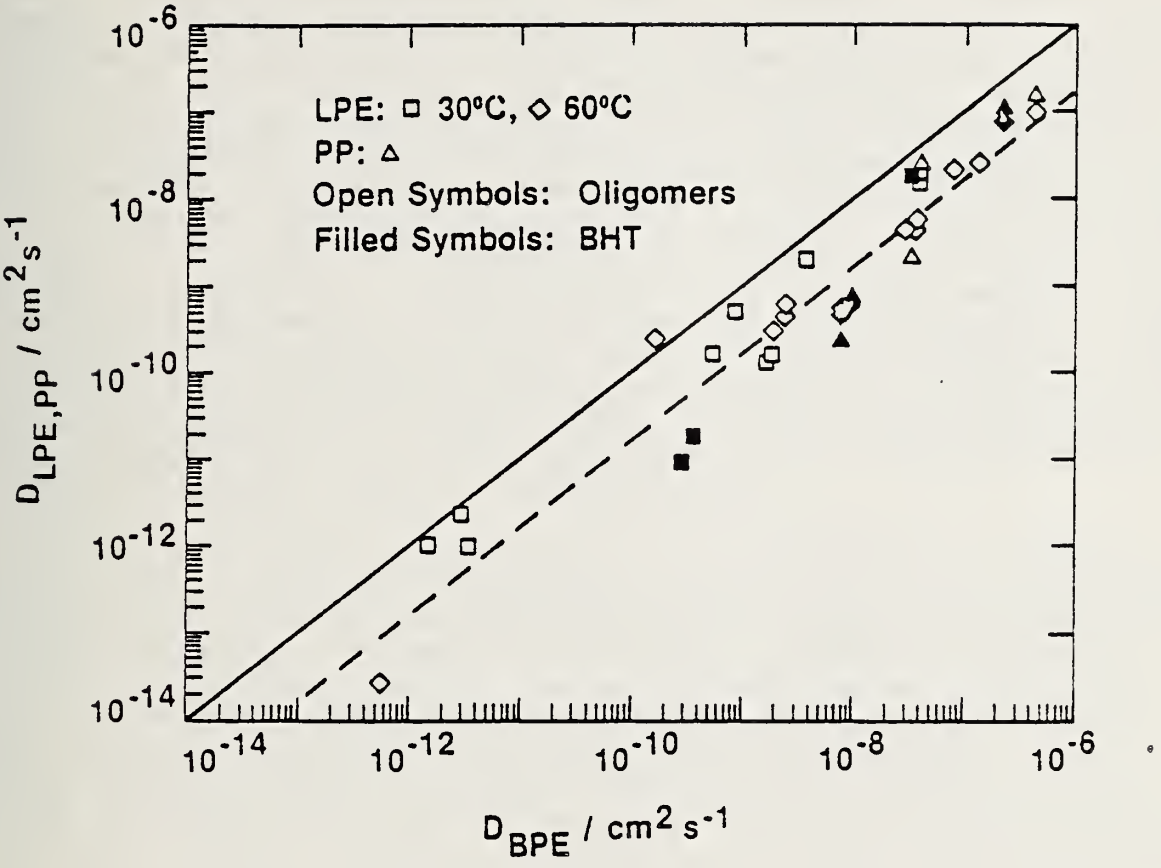
LPE: □ 30°C, ◇ 60°C
PP: △
Open Symbols: Oligomers
Filled Symbols: BHT
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
$D_{LPE,PP}$ / $cm^2 s^{-1}$
D_{BPE} / $cm^2 s^{-1}$

Figure 3

DIELECTRIC AND PIEZOELECTRIC PLASTICS DESIGN AND PERFORMANCE
Task 12139

Trends in dielectric application of polymers include use of higher working voltages in electrical apparatus and transmission lines to conserve materials, save space, and reduce weight. This work provides manufacturers (polymer manufacturers, film fabricators, transducer manufacturers), trade associations (EPRI), and Government agencies (DOE, DOD) with data, measurement methods, and concepts which identify limitations in polymer performance traceable to manufacturing practices. For example, steam curing of extruded polyethylene insulated cable results in lifetime-limiting voids and inclusions. With a trend toward increased use of underground transmission of electric power, improved insulation performance is required. To meet these needs, NBS develops measurement methods and performs measurements to obtain required data, holds workshops to improve research efforts in the area of power cable and capacitor insulation, recommends test methods for new material selection, and carries out related activities. Data and recommendations from this work go directly to cable manufacturers and funding organizations (i.e., EPRI, DOE) who are able to specify and require manufacturing changes leading to improved products.

Applications of polarized polymers as pyro- and piezoelectric transducers are rapidly growing. Transducer manufacturers as well as private and Government transducer users (DOD, EPA, HHS) need reliable information connecting polymer structure and polymer performance to the design of improved transducers. This work will help transducer material and device manufacturers design and develop commercial polymer transducers for use in health and safety applications (pulse monitors, therapeutic and diagnostic sound measurements, auto crash sensors, prosthetic fitting devices, nontoxic antifouling coatings, mine disaster warning devices), and in the areas of national security (microphones, hydrophones, intrusion detectors, ultrasonic and infrared imaging devices, fusing devices, etc.). Important scientific opportunities of this work include breakthroughs in understanding the basic factors in electrical failure of polymers and discovery of novel measurement methods which are becoming possible with newly developed polymers. For example, this work attempts to show how polymers interact with electronic and ionic charges and how structure can be modified to optimize piezoelectric and semiconducting properties.

The study of electrical conduction of organic polymers is a major new frontier in solid state physics. Most current research involves an empirical search for improved dopant-polymer combinations from a bewildering array of compounds. Chemical structure-electrical property correlations are not yet evident. The key need is for a better knowledge of the molecular packing, dopant locations, chemical changes with doping, molecular orientation, and charge carrier pathways to form a basis for modeling and predicting electrical properties. This work is ideally suited to NBS because it involves improved measurements, standards, and test methods. Polymer conductors have the advantages of being lightweight, flexible, abundantly available, resource and energy conserving, and inexpensive. Thus, success of the project will have a potentially significant impact on national problems of materials replacement, productivity enhancement, energy conversion and storage (polymer batteries), electromagnetic shielding, and microcircuitry.

Ionic conduction in polymers provides a basis for a large and growing class of important applications including production of chlorine and caustic from brine, hydrogen production from low-head hydroelectric or ocean thermal energy sources, solid electrolytes for fuel cells and batteries, gas sensors, materials separation membranes, and electrochemical devices. NBS work on conducting polymers is aimed at characterizing the polymer structures, measuring their properties, and relating the structures and properties to provide a basis for predicting electrical performance from molecular details.

Polymer Tape Insulation for Oil Impregnated AC Power Transmission Cables
Subtask 1 of Task 12139

F. A. Khoury, F. I. Mopsik, S. J. Kryder, L. H. Bolz

Brookhaven National Laboratory has established a program to develop an oil impregnated or oil filled high power ac transmission cable using polymer tape insulation. Until now, oil impregnated paper has been used for large power cables, but the relatively high loss of such cables has generated interest in lower loss systems, such as oil-polymer cables for use at 700 to 1000 kV.

A project sponsored by Brookhaven with DOE funds has been established in the Polymer Science and Standards Division to evaluate the suitability of polymer films. The aims of this project are: the measurement of the dielectric constant and dielectric loss of candidate films between 273 K and 403 K, the study of the fine structural characteristics of the films, and the specification of the most suitable films for the intended end use. Brookhaven uses the NBS data to select the most suitable film, or to order specially oriented or bonded films, for new synthetic-tape-insulated power cables. The development of such cables has been identified by EPRI as an important short-term research objective in meeting increasing U.S. electric power requirements.

Measurements this past year have been carried out on polyethylene and polypropylene tapes prepared for Brookhaven by Battelle Institute. They were prepared by rolling at temperatures from 293 to 398 K for polyethylene with thickness reduction ratios of four to ten and at a temperature of 423 K for polypropylene with thickness reduction ratios of five to six. Two different base polymers were used for both the polyethylene series and the polypropylene series. The dielectric measurements were carried out under standard temperature cycling, and density measurements were carried out on the tapes both before and after the dielectric measurements to check on their stability under thermal cycling.

All the polyethylene tapes showed a stong decrease in loss on thermal cycling. The decrease at 303 K (after heating to 373 K) was about a factor of two. Aside from this decrease, the losses in one base polymer were substantially lower than in the others (less than 24×10^{-6} on the third heating cycle). All the tapes increased in density with thermal cycling, but the tapes rolled at 398 K showed a much smaller change showing increased mechanical stability.

The polypropylene tapes, which were processed at a roll temperature of 423 K (the maximum temperature of the dielectric measurements) showed a different behavior depending on which of two base polymers was used. Tapes made from one base polymer showed little variation with thermal cycling and a loss maximum at 350 K of 35×10^{-6}. Tapes made from the other polymers showed a

loss peak that shifted with thermal cycling from 320 K to 370 K with a maximum value of about 800 x 10^{-6}. Tapes from both polymers showed an increase in density after the thermal cycling, showing that they had not been fully stabilized at the rolling temperature.

This project was completed during FY81 and a final report was prepared.

Polymer Insulation for Superconducting AC Power Transmission Cables
Subtask 2 of Task 12139

F. A. Khoury, F. I. Mopsik, S. J. Kryder, L. H. Bolz

This project is funded through Brookhaven National Laboratory by DOE. The goal has been to evaluate the suitability of polymer films for use as electrical insulation in a superconducting ac power cable that would operate at 6.0 to 8.0 K. Development of a superconducting power cable has been identified by EPRI has a long-range research goal in order to meet future demands for very high power transmission (several giga watts). The measurements done by NBS have enabled Brookhaven to specify special composite tapes which are now being built into prototype cables.

The primary task in this project has been the measurement of the dielectric constant (ε) and dielectric loss ($\tan \delta$). These should be less than 2.5 and 20 x 10^{-6} at 6.0 to 8.0 K and 60 Hz for suitable insulation. These measurements have been coupled with studies of the fine structure of the films (crystallinity, molecular orientation, voids) to guide the development of optimal films. In addition, measurements of the compressibility of stacks of polymer films have been made to provide data necessary for winding the films (sliced into tapes) onto the cable core.

In FY81, measurements were made on a series of laminates made from polypropylene films of 40 to 60 μm thickness bound together by thin polyurethane layers to provide total thicknesses of 80 to 180 μm. These laminates have shown promise of meeting all necessary requirements in work done in previous years. One series of measurements was made on a set of laminates graded in thickness. Three were bilaminates of total thickness 80, 100, and 120 μm. All the films had suitably low loss levels with tan δ ranging from 10-15 x 10^{-6}. Low loss was achieved by use of a polypropylene film that had low loss antioxidants as well as reduced polyurethane content. Previous work had shown that antioxidants can strongly increase the loss of polypropylene at cryogenic temperatures of 10 K and below. Also, it had been shown that if too much polyurethane was used as a binder, the higher loss levels of the polyurethane could deteriorate the performance of the laminates.

Another series of measurements was made on a bilaminate 94 μm thick and a trilaminate 140 μm thick in which a slip agent had been added to the polypropylene in order to obtain better mechanical properties of the finished cable. Losses increased to 16 to 23 x 10^{-6} at 6.0 to 8.0 K as a result of this change.

In addition to the dielectric loss measurements, compressibility measurements were made on stacks of the first set of laminates, carbon loaded polytetrafluoroethylene, and carbon loaded Kraft paper. These data are needed to insure proper bendability of a finished power cable.

This project has been completed and funding for further research on the insulation for the superconducting cable terminated. A prototype cable is being built.

NBS Workshop on Morphological Studies of Power Cable Insulation Failure
Subtask 3 of Task 12139

M. G. Broadhurst, F. A. Khoury, A. J. Bur, G. T. Davis

Experts on the morphology of polyethylene were among those gathered at NBS for a two-day workshop to define the current state of research on the causes of premature failure of polyethylene insulation for high power transmission cables. This Workshop on Morphology was organized by Martin Broadhurst of the Polymer Science and Standards Division and was jointly sponsored by NBS and the Electric Power Research Institute, the research arm of the U.S. electric utilities. Participants came from electric utilities, cable makers, polymer manufacturers, and universities. In the welcoming address, J. D. Hoffman, Director of NML, described his research and its relevance to both the electrical properties and morphology of polymers. NBS scientist Freddy Khoury delivered the keynote address.

The electric utilities requested this workshop because of their continuing concerns for reducing costs and improving efficiency of electrical transmission systems. A further concern is to minimize space required for power transmission and the environmental impact of transmission lines; both of these considerations favor underground cables, and polymer-insulated cables operating at higher voltages are attractive solutions. But improved dielectric performance and durability are required.

Several scientific approaches to correcting the problem of electric failure in polymers are currently being used. In one promising new approach, morphologists use electron and optical microscopes along with other techniques to examine structural details of the polyethylene cable insulation to deduce reasons for failure and to identify ways to modify processing conditions to achieve better performance. Recent studies have been at odds as to how failure channels which develop during cable operation are related to the chemicals and steam used to cross-link or cure the insulation. There was a consensus that the various etching techniques now being used in cable insulation studies often produce artifact structures on the surface of polyethylene samples which are not representative of the original samples. Many structural interpretations are, therefore, in doubt. Improved methods of carrying out these important measurements to give more reliable results were delineated.

A summary report of the workshop has been prepared by NBS to be issued as an EPRI publication. This report will be used immediately by EPRI as a guide to planning and funding future research projects on morphology of polyethylene insulated cables. In the longer term, this work will lead to improved processing conditions and better performance from underground electric power cables.

Space Charge Studies
Subtask 4 of Task 12139

A. S. DeReggi, F. I. Mopsik

The measurement of charge distributions in solid polymers is basic to understanding polymer-charge interactions. These interactions may play a key role in a material's insulating or conducting properties, electrical strength, and electrical aging. This NBS perfected method has recently found enthusiastic acceptance at industrial laboratories such as Bell Labs where charging is a key factor in new electret telephone systems.

During the past year, the thermal pulse method has become increasingly accepted as one of the most powerful, readily-available methods for measuring the distribution of charge or polarization in a dielectric film as a function of depth, where the thickness of the film is of the order of 25 μm (0.001 in). Moreover, the theoretical approach developed at NBS for analyzing thermal pulse data has been shown by actual numerical computation to give about 10 Fourier coefficients of the charge or polarization distribution. The form of a polarization distribution obtained by a thermal pulse experiment has, thus, the accuracy of a Fourier series summed to around 10 terms. The procedure for analyzing thermal pulse data now has been computerized to the extent that our minicomputer receives digitized thermal pulse data via a tape cassette and outputs a graph of the polarization distribution. These developments have been presented in the proceedings of the most recent Conference on Electrical Insulation and Dielectric Properties in Boston (1980), and a more extensive article is in review.

The above progress in data analysis has opened the possibility of obtaining for the first time quantitative and unambiguous information about polymer charging phenomena. For instance, we have shown that the piezoelectric polymer, polyvinylidene fluoride (PVDF), when poled at ambient temperature, poles more or less symmetrically but not uniformly. The regions near the surfaces seem to have a greater reluctance to responding to applied poling fields than the bulk of the sample. This is manifested in the evolution of the polarization distribution under progressively stronger mean applied fields in the thickness direction followed by progressively stronger reverse applied fields. At low forward fields, the polarization in a virgin sample first forms in the bulk. At medium and high fields, it develops near the surfaces in addition to the bulk. Up to the highest attainable fields, it remains somewhat less ($\sim$ 15 percent) near the surfaces than in the bulk. When the applied field is subsequently reversed, the polarization reverses in the bulk more readily that it does on the surface. A sample which is forward poled at 2.0 MV/cm and subsequently is reversed poled at -1.0 MV/cm exhibits strong forward polarization near the surfaces and strong reverse polarization in the bulk, with practically zero mean polarization.

These effects are believed to be due to the mechanical constraints imposed during poling by the deposited aluminum electrodes. Investigations now underway will provide additional information concerning the origin of the above effects. These investigations include studies of the dependence on thickness of the Al, thickness of the polymer, and on the type and thickness of the electrode material.

The effects on charging phenomena associated with work function differences between the polymer and metal electrode are also of basic interest and could be important in determining poling behavior. Previous qualitative thermal pulse work at NBS on non-polar polymers strongly indicated differences in charging properties when Al and Ag were used as electrode materials. During a renewed visit to NBS, contractor Prof. Sidney Lang of the Ben Gurion University has been studying the effects of electrode material in the polarization distribution in PVDF poled over a range of applied fields.

We also have begun to apply the thermal pulse method to investigate charging of polymers bombarded by electron beams. These studies have been motivated by interest at Rome Air Development Center on the electron-beam charging of polyvinyl chloride films. Simple models for the radiation effects on the conductivity which are currently being developed at RADC predict nonuniform distributions. To guide this theoretical work, there is a need for experimental determinations of the charge distribution. Our thermal pulse measurements, so far, for 700 kV electrons and a limited dose range (200 to 2000 seconds at 10^{-9} A/cm^2) indicate more or less uniform charge distributions at long times after irradiation.

Structure and Performance of Piezoelectric Polymers
Subtask 5 of Task 12139

G. T. Davis, M. G. Broadhurst

The objectives of this task are to study the molecular motions, structural changes, and electrical properties associated with the process whereby polymers are made piezoelectric. Information gained from these studies will be used to optimize piezoelectric and pyroelectric response with respect to both initial activity and long-term stability.

While piezoelectric and pyroelectric activity from polymers is comparable to that from good ceramic materials, other properties of polymers often make them the preferred transducer material. Some of the polymer properties which make them so useful include toughness, flexibility, low density, broad band response, close acoustic impedance match to water, and ease of fabrication. Requests for information from other Government agencies and from industries have remained numerous. Interest in this area of research continues at a high level, as evidenced by the 22 papers on this topic presented at the American Physical Society meeting in March 1981.

A copolymer of vinylidene fluoride and trifluoroethylene (52.8 mol % VDF) has been studied in terms of structural changes that occur upon poling and subsequent depoling by heating through the reported ferroelectric Curie temperature of 70 °C. As crystallized from the melt, the polymer is a mixture of two phases. In one phase, the molecular conformation is thought to be $(TG)_3$, resulting in a 3/1 helix as in the trifluoroethylene homopolymer. In the other phase, the molecular conformation is all trans, in which the molecules are packed hexagonally. The electric fields employed in poling (0.5 to 1.0 MV/cm) are sufficient to cause a crystal phase conversion to the all trans conformation with considerable improvement in order, as evidenced by a shift to smaller cell dimensions and sharper x-ray diffraction maxima. Upon heating, the two coexisting phases

initially present undergo large changes in cell dimension between 60 and 70 °C, and only a single 3/1 helical conformation exists above 85 °C. Although the change in conformation from all trans to $(TG)_3$ which occurs in the vicinity of 60 to 85 °C, can certainly account for the ferroelectric transition; much of the piezoelectricity induced by poling at room temperature is lost before the transition to a single 3/1 helical conformation is observed. It, therefore, seems probable that polarization is lost by randomization of the dipole direction followed by a change in chain conformation at a somewhat higher temperature.

We have succeeded in varying the small angle x-ray spacing in drawn samples of polyvinylidene fluoride by adjusting the temperature of extension--a processing characteristic reported years ago for polyethylene and polypropylene. The linear position-sensitive detector on the Rigaku Denki rotation anode source was employed to measure long spacings varying from 11.5 nm to 16.5 nm. These films were prepared to study the effect of lamellar spacing on the poling characteristics of PVDF. Over this range of crystal size, there is no effect on the pyroelectric response for poling fields in excess of 2.0 MV/cm. The ease of switching as determined from hysteresis loops has yet to be measured.

Dielectric and polarization data were compared to calculated results from a ferroelectric theory developed in our laboratory. The model has six equally spaced rotational energy minima. A first-order cooperativity assumption is applied, and the dielectric constant and remnant polarization are calculated as a function of temperature. Comparison between the experimental and calculated results gave good agreement.

Aging of Piezoelectric Polymers and Application to Biomedical Uses
Subtask 6 of Task 12139

D. E. DeRossi, S. C. Roth, A. S. DeReggi, M. G. Broadhurst

A new research associate in the Polymer Science and Standards Division has begun work on the aging and durability of piezoelectric polymers for biomedical devices under sponsorship of the Brown University Research Foundation. Dr. Danilo DeRossi, on leave from the University of Pisa where he is on the Faculty of Engineering and a Group Leader in the Institute of Clinical Physiology, sees great potential for such polymers in biomedical uses and has come to NBS to develop measurements of and models for the aging of piezoelectric activity in polymers.

The unique properties of piezoelectric polymers--low density, good mechanical impedance match to human tissue, flexibility, nontoxicity, and ease of fabrication in complex patterns and arrays--are ideally suited to biomedical transducer applications. The factors which affect the stability of the piezoelectric activity in polymers are not well understood, however, nor are accelerated tests available to measure the durability of piezoelectricity in these materials. This Research Associate Program will include the following activities: laboratory research to improve techniques for periodic nondestructive measurements of the performance of piezoelectric polymer samples, experiments to aid in the development of an accelerated service test to facilitate evaluation of the relative durability of piezoelectric polymers, design and evaluation of predictive mathematical models relating the molecular and microstructural characteristics of piezoelectric polymers to aging mechanisms, and evaluation and recommended improvements of existing methods for calculating the properties of polycrystalline samples (the commonly available form) from analyses of single crystal results.

Through this program, fundamental polymer transducer science at NBS will be transferred to Brown University and other private sector groups which are inventing and developing devices. NBS will gain assistance and impetus from their efforts to develop and improve test methods, data, and concepts regarding durability and aging in the important new class of piezoelectric polymer materials.

This current activity is expected to be followed by other research associate activities related to the use of polymer transducers in areas such as robotics.

Automated Dielectric Measurements
Subtask 7 of Task 12139

F. I. Mopsik, S. J. Kryder, S. C. Roth

This subtask was begun as part of the power cable insulation subtasks (1 and 2) to meet the need for more rapid dielectric measurements on large numbers of samples. The instrument being developed will record the transient electric charge response of a dielectric sample to a step change in electric field in real time. This response will automatically be transformed into dielectric constant and loss over the frequency range of 10 kHz to 1 mHz and plotted by computer. The work directly supports Task 12139 by providing a basic tool for measuring electrical properties.

During FY81 the electronic circuits for an automated dielectric spectrometer were completed. A hardware clock programmer was built to allow for compatiblity between the sampling rates needed at the beginning of the transient and the time the computer needs to make changes in the operating conditions during data acquisition. This device provides automatic sequencing through the first of three sampling rates so that the computer has time to take control of the sampling.

The analog-to-digital converter has been built and tested. The converter has successfully operated at speeds compatible with a 5 μs sampling time so that the beginning of the transient can be well characterized and extrapolated to the beginning of the charge transient. Its sensitivity and noise level is such that it will not degrade the performance of the charge detector.

Finally, the first few data acquisition programs have been written, and the interfaces of the components (generator, detector, converter, clock, clock programmer) to the computer have been successfully tested. The initial results show that the desired loss sensitivity (< 10 μrad) can be achieved and that the design goals will be met. The resolution was sufficient to show that one of a pair of 10 pF standard capacitors was faulty and had an apparent negative loss that was confirmed by transformer bridge to be -70 μrad at 100 Hz. For the size of the integrating capacitor used in the detector, this result was well within the sensitivity limits initially desired.

Depolarization of Poled PVDF Specimens With Thick Electrodes
Subtask 8 of Task 12139

A. J. Bur, A. K. Tsao

The effect of electrode thickness on the activity of thin film PVDF was investigated by observing the pyro- and piezoelectric activity of 26 specimens whose electrode thickness varied from 60 to 310 nm. These samples were obtained from Bell Laboratories (Allentown, Pennsylvania) where they were poled under uniform conditions after the entire electrode was deposited on the sample. This subtask was done partly in cooperation with Bell Laboratories who are interested in the effects of electrode thickness for telephone switch pad devices and contributes to the NBS task of optimizing transducer material for applications.

The electrodes consisted of two layered metals: first, Ti was deposited to a thickness of 60 nm; Au was then deposited on top of the Ti to a thickness which varied from 15 to 250 nm.

The samples were examined in three experiments: (1) the hydrostatic piezoelectric coefficient, d_p, and the pyroelectric coefficient, py, were measured for the original samples; (2) d_p and py were measured after the thick electrodes were removed; and (3) the depolarization charge was measured by detecting the discharge as the samples were subjected to an abrupt temperature rise through the melting point. For the second experiment, all samples had Ti electrodes of 60 nm thickness. The results of these measurements are: (1) the values of d_p and py for the as-received samples were lower the thicker the electrode; (2) with the thick electrodes removed from the samples, the values of d_p and py were the same as those for the thick electrodes in place; and (3) the depolarization charge decreased as the original electrode thickness increased.

We have concluded that the decrease in d_p and py as a function of electrode thickness is essentially due to the decreases in polarization of the thick electroded specimens and that thick electrodes mechanically constrain the sample during poling so that optimum poling cannot be achieved.

Fabrication of Thick Piezoelectric Polymer Film
Subtask 9 of Task 12139

A. J. Bur, M. G. Broadhurst, A. K. Tsao

The subtask results from a direct request from the Navy to explore fabrication of thick piezoelectric polymer film for hydrophone use. Thick film is needed because the voltage response of thin PVDF films is less than typical ceramic hydrophones. The voltage response is inversely proportional to capacitance and hence directly proportional to the thickness of the film. To make the voltage sensitivity of polymers better than that of ceramics the thickness should be at least 750 μm. To stretch and polarize a film this thick requires special equipment and so far only a couple of European companies have been successful at producing it. In this work, NBS is developing techniques whereby industrial laboratories in the U.S. can produce suitable films.

Ultra-drawn PVDF is material which has been stretched beyond its natural draw ratio of 4:1. Using a PVDF sample which had been previously stretched to its natural draw ratio of 4:1, it is possible to obtain draw ratios of 6.5 or 7.0 to 1.0 by reclamping the sample in the Instron machine and stretching at 140 °C at a rate of 0.05 in/min. During the ultra-stretch, the load increases while the sample dimensions decrease, indicating that the modulus increases with increasing draw ratio. The ultra-drawn material is desired because it contains mostly β phase material, it is highly oriented, and it is able to withstand high poling fields.

Poling these thick samples requires high voltages. For example, to pole a 0.3 mm thick sample at 2.0 MV/cm, 60 kV are needed. Working at these voltages, it is necessary to suppress corona and flashover conduction by carrying out the poling in oil and to construct the sample electrodes so that high electric fields are not present at the edges.

Acoustic Sensors
Subtask 10 of Task 12139

A. S. DeReggi, S. C. Roth, S. Edelman

Probing hydrophones and biomedical sensors made with the piezoelectric polymer polyvinylidene fluoride (PVDF) have been shown to have superior performance characteristics over previously available piezoelectric ceramic devices in terms of a wide operating band-width and negligible insertion effects. These favorable characteristics stem from the similarity in acoustic impedance between the PVDF and the common transmission and test media relevant in ultrasonics, such as water and oils, and in the case of biomedical ultrasonics body tissue. There is currently a growing interest in these polymer transducers in the ultrasonic community in general and in the biomedical community in particular. The collaboration between NBS and a guest worker from the Bureau of Radiological Health (BRH) has continued during the past year. The principal aims of the collaborative work are the development of polymeric acoustical probes for measuring the radiation pattern of biomedical transducers and the development of improved methods of characterizing the performance of existing biomedical transducers using the new polymeric probes. The knowledge obtainable with the new polymeric sensors can be used to ensure both the safety and adequacy of ultrasonic dosage as well as to advance research in ultrasonic treatment.

A variety of ultrasonic probing hydrophones and hydrophone arrays have been constructed, all featuring the spot-poled, tensioned membrane design configuration which was introduced at NBS several years ago and was publicized extensively during the course of the past year through contributions to the Proceedings of the 25th Annual Meeting of the Institute of Ultrasound in Medicine (September 1980), the 1980 IEEE Ultrasonics Symposium (November 1980), the Sixth International Symposium on Ultrasonics Imaging and Tissue Characterization (June 1981), and through the publication of an article [1]. In addition, BRH has filed a patent application (November 1980), and NTIS has publicized this patent application among ultrasonic manufacturers who might be interested in its commercialization.

The typical active electrode diameter of these probes is around 1.0 mm, although useful output has been obtained from a probe with an active electrode diameter as small as 300 μm. The operating bandwidth of greatest interest is 0.5 to 5.0 MHz. Over this range, the frequency response of the polymer sensors is flat, with a sensitivity for a probe with a 1.0 mm diameter active electrode of -237 dB ± 1.5 dB re 1.0 V/μPa, and an insertion loss not exceeding 2.5 dB. Repeated sensitivity measurements over a period of 2.5 years have indicated good stability with no credible trend for reduced sensitivity within the ± 1.0 dB accuracy of the measurements.

Larger diameter (1.0 cm diameter active area) piezoelectric polymer sensors have been used at NBS for many years to demonstrate the capability of piezoelectric polymers to detect the heart pulse when held against the skin at the medically common peripheral monitoring sites. In collaboration with NBS, members of the CNR Institute of Clinical Physiology at the University of Pisa are evaluating piezoelectric sensors for the monitoring of cardiac patients.

Preliminary clinical data on peripheral pulse signals obtained at Pisa with NBS sensors will be presented at the forthcoming Computers in Cardiology Conference in Florence in September 1981. These data appear to give information complementary to but not necessarily contained in EKGs.

Reference:

[1] A. S. DeReggi, S. C. Roth, J. M. Kenney, and S. Edelman, J. Acoust. Soc. Am. 69, 853 (1981).

Polymer Stress Gauge for Intaglio Printing Press
Subtask 11 of Task 12139

M. G. Broadhurst, S. C. Roth, S. J. Kryder, A. S. DeReggi, S. Edelman

This work is supported by the Bureau of Engraving and Printing, U.S. Department of Treasury. The purpose is to develop a gauge to measure the dynamic pressure at critical points in the presses used to print money. The first phase of the work is completed. The accomplishments of the first phase included measurement of the width of the area of contact between the two cylinders of the press, the duration of contact of a point on the upper cylinder with the lower cylinder, and a qualitative (uncalibrated) determination of the change of the pressure with time during contact.

The second phase of the work is to provide a calibrated pressure transducer and a complete signal processing system for transmitting the transducer signals from the operating printing press and providing pressure and temperature vs time data for the nip (region of contact between the printing rollers). Piezoelectric polymer strips containing a pressure tranducer and thermocouple are placed under the fiber rigging on the top roller of the press. When the polymer strip moves into position between the top and bottom rollers, it is subjected to both a pressure increase and a temperature increase due to adiabatic heating of the trapped and compressed air. The thermocouple signal monitors the temperature change, and the signal processor subtracts from the polymer transducer signal that part which is due to temperature change. The resulting signal is that due to pressure change only. A calibrator has been developed

to monitor and correct for changes in transducer response due to aging while the transducer is installed on the press. A final check of the system has been performed between metal plates covered with rigging material and mounted in a hydraulic press. Sudden release of pressure in the hydraulic press simulates the release of pressure in the printing press as the nip moves past the transducer. The pressure measurement system will provide the BEP with data on printing pressures and temperatures which will not only permit better control of printing pressures but also will provide data needed for improving paper and ink.

Successful demonstration of this measurement technique has received the attention of both the paper and synthetic polymer film manufacturers who have a long-standing need to measure and control pressures between the rollers used to make films. Results will be transmitted to these industries.

Resistivity and Piezoelectric Measurement on Oriented and Unoriented PVDF Films
Subtask 12 of Task 12139

A. J. Bur

This subtask directly supports the optimization of piezoelectric polymers for applications in industry and Government. It concerns that part of the transducer preparation where large electric fields are applied to the film in order to polarize it. It has been found that the larger the field, the higher the piezo/pyroelectric activity and this subtask examines the effect of film orientation on the maximum electric field which the material can support.

Thick specimens of PVDF were prepared by molding PVDF powder or pellets in a compression mold under vacuum. These specimens, in an isotropic unoriented condition, were found to be unsuited for poling because electrical breakdown occurred at fields between 0.3 and 0.6 MV/cm, which are too low to produce significant polarization. When these samples were mechanically oriented, however, poling fields of 1.0 MV/cm or higher could be attained so that acceptable transducer activity could be achieved. This much orientation was carried out by means of tensile extension at 55 °C which produced a natural draw ratio of 4:1.

In order to examine the difference between the electrical properties of mechanically oriented and unoriented PVDF, we measured resistivity before and after orientation. The resistivity for an oriented sample at room temperature showed a marked rise by an order of magnitude or more above that of the unoriented samples. For unoriented samples, resistivities were in the range 1.7 to 2.4×10^{15} ohm-cm, whereas for the oriented samples resistivities ranged from 4.2×10^{16} to $> 2.2 \times 10^{17}$ ohm-cm.

While we did not establish a correlation between resistivity and electrical breakdown voltage, we have established that poling fields of 1.0 MV/cm and higher are not possible unless PVF_2 is mechanically oriented. With this knowledge, we have been able to fabricate thick (0.5 mm) PVF_2 transducers.

Nondestructive Evaluation
Subtask 13 of Task 12139

S. Edelman, S. C. Roth

A method for nondestructive evaluation and the dynamic elastic properties of some kinds of structural elements was worked out during previous years, and a paper on the subject was presented at the Spring 1980 meeting of the Acoustical Society of America. The measurement technique made use of the favorable properties of piezoelectric polymer strain gauges to measure both axial and shear motion on the same specimen. The specimen can be evaluated nondestructively while it is in service. This subtask demonstrates to potential manufacturers this important application of piezoelectric polymers and is supported by the NDE program at NBS.

During this reporting period, a set of the specialized piezoelectric strain gauges required by the method was fabricated. The gauges were mounted on a thin-walled PVC cylinder which simulated a structural element under load.

Several measurements were made at different frequencies. The real and the imaginary parts of the dynamic Young's modulus were calculated. Reasonable agreement with published values of the real part was found. The results of two sets of measurements at slightly different frequencies are given in the table below. Each set consists of three nominally identical measurements.

Frequency	α (m^{-1})	β (m^{-1})	E_1 (Pa)	E_2 (Pa)
6915	3.19	27.33	3.37×10^9	7.97×10^8
	3.19	27.32	3.37×10^9	7.99×10^8
	3.19	27.33	3.37×10^9	7.99×10^8
6836	2.82	27.36	3.32×10^9	6.91×10^8
	2.82	27.38	3.31×10^9	6.92×10^8
	2.83	27.38	3.29×10^9	7.45×10^8

α and β are the attenuation and phase constants which make up the propagation constant where $\gamma = \alpha + \beta$ and where γ is related to the wave amplitude ξ_x by the relation $\xi_x = \xi_0 e^{-\gamma x}$.

E_1 and E_2 are the real and imaginary parts of the Young's modulus, $E = E_1 + iE_2$.

Measurements are presently being made on a section of pipe while the pipe is subjected to a changing tensile stress.

ASTM Activities
Subtask 14 of Task 12139

W. P. Harris

This involvement in ASTM is one method by which the task output impacts the industry. Mr. Harris attended the October 1980 and March 1981 meetings of ASTM Committee D-9, Electrical Insulating Materials. He continues to be active in several subcommittees, especially in the area of electrical measurements. He is also active on the Executive Subcommittee, which is responsible for governing the main Committee.

The Crystal Structure and Disorders of the Low Temperature Phase (II) of Polytetrafluoroethylene
Subtask 15 of Task 12139

J. J. Weeks, E. S. Clark[1], R. K. Eby, B. L. Farmer[2]

[1]University of Tennessee.
[2]Washington State University

Long-term durability studies of a series of polymers revealed that fluoropolymers had superior stability of dielectric and mechanical properties. Therefore, they were chosen to make standard reference materials for calibration of industrial dielectric cells. As noted below, this has indeed turned out to be the case. To investigate the origin of this superior stability, we have carried out studies of the crystal structure.

An electron diffraction pattern from polytetrafluoroethylene in Phase II was analyzed to determine a chain conformation of 2.1598 CF_2 units per turn of the helix. A structure was established from a combination of electron and x-ray diffraction data. The structure contains an ordered repeating pattern of a left- and right-handed pair of chain stems. Although the structure is ordered in three dimensions, it cannot be described meaningfully in terms of classical space group nomenclature because very small changes in the structure result in very large changes in the cell parameters. The structure has a volume of 0.03542 nm^3 per CF_2 group, corresponding to a density of 2344 kg/m^3.

Energy analysis was used to determine the low energy crystal structure for polytetrafluoroethylene molecules in the 13/6 and 54/25 conformations. The structure for the 54/25 conformation contains an ordered repeating pattern of a left- and right-handed pair of molecules in a unit cell having projected parameters, a', b', and γ', of 9.60 Å, 5.62 Å, and 91.4 degrees, respectively. These results, the relative orientations of the molecules, and the relative translations of the molecules are in good agreement with results obtained in a concurrent and independent analysis of diffraction data. Energies calculated for rotational and translational displacements in various modes suggest that a range of structures and a fairly large amount of disorder may be present, also in agreement with experiment.

X-ray diffraction patterns for oriented and unoriented copolymers of tetrafluoroethylene and hexafluoropropylene were obtained. They show a transition between 229 and 243 K for a copolymer with about 3.4 CF_3 per hundred main chain carbon atoms. The lower temperature phase (II) appears to be similar to that of the homopolymer. A primary difference is the presence in the copolymer crystals of small longitudinal displacements of the molecules caused by the randomly located CF_3 groups. The displacements increase with increasing CF_3 concentration. The higher temperature phase (I) is similar to that of the homopolymer with a difference again being the longitudinal disorder of the copolymer. The difference disappears at higher temperatures as longitudinal disorder is introduced thermally in the homopolymer. At 296 K (phase I), the molecular stems in a copolymer with about 3.4 CF_3 per hundred main chain carbon atoms are at an angle of 37.1 degrees with respect to the normal to the basal plane of the lamellas. In phase II, this number is the same within the limits of error.

Other Activities of the Polymer Science and Standards Division

Invited Talks

Linear Dimensional Change for Zinc and Non-Zinc Containing Amalgams During Storage in Air at 60, 37, and 23 °C
International Association for Dental Research, Chicago, Illinois
G. C. Paffenbarger
June 6, 1980

Consideration of Some Factors Influencing Compatibility of Dental Porcelains and Alloys
Fourth Annual Meeting of the International Precious Metals Institute, Toronto, Canada
J. A. Tesk, R. P. Whitlock, G. E. O. Widera, A. D. Holmes, and E. E. Parry
June 8, 1980

Recent Developments in Adhesive Resin Formulations for Dentin
International Congress of Implantology and Biomaterials in Stomatology, Kyoto, Japan
R. L. Bowen
June 10, 1980

A Mean Field Theory of Polymer Solutions
International Symposium on Phase Transitions in Polymers, Cleveland, Ohio
I. C. Sanchez
June 11, 1980

Achieving Excellence With Modern Dental Materials
Kootenai Study Club, Libby, Montana
N. W. Rupp
June 26, 1980

Recent Developments in Dental Materials
Dentsply International Inc., York, Pennsylvania
N. W. Rupp
July 23, 1980

Selection and Manipulation of Dental Materials
Wilford Hall Dental Center, San Antonio, Texas
N. W. Rupp
August 7, 1980

Dynamic Light Scattering of Polymer Solutions in Dilute Region
Joint U.S.-France Symposium on Small Angle Neutron and X-ray Scattering, Strasbourg, France
C. C. Han
September 23, 1980

Selection and Use of Dental Materials
Eglin Air Force Base, Florida
N. W. Rupp
September 23, 1980

Developments in Composite Resins
Howmedica Biomaterials Seminar, Groton, Connecticut
R. L. Bowen
September 24, 1980

Overview of the Polymer Science and Standards Division
Environmental Protection Agency, Cincinnati, Ohio
R. K. Eby
September 26, 1980

Applications of High Resolution ^{13}C NMR Techniques to Polymers
Akron University, Akron, Ohio
D. L. VanderHart
October 3, 1980

Restorations of the Future
Academy of Gold Foil Operators, New Orleans, Louisiana
N. W. Rupp
October 10, 1980

Modifications in Cavity Preparation Using Acid Etch Techniques
American Dental Association Annual Scientific Session, New Orleans, Louisiana
N. W. Rupp
October 14, 1980

Statistical Thermodynamics of Fluid Mixtures
Ecole Nationale Superieure des Mines, Paris, France
I. C. Sanchez
October 20, 1980

Molecular Origins of LCST Behavior in Polymer Solutions
CEN de Saclay, Gif-sur-Yvette, France
I. C. Sanchez
October 21, 1980

The Diversity of the Habits of Polyethylene Crystals Grown From Solution
Cornell University, Ithaca, New York
F. A. Khoury
October 23, 1980

New Developments in Restorative Dentistry
Navy Dental School, Bethesda, Maryland
N. W. Rupp
October 23, 1980

Equation of State Theories of Polymer Blends
Centre de Recherches sur les Macromolecules, Strasbourg, France
I. C. Sanchez
October 23, 1980

Mettler Award Address
Tenth North American Thermal Analysis Society, Boston, Massachusetts
J. H. Flynn
October 27, 1980

New Developments in Composites
Dental Study Club, Washington, D.C.
N. W. Rupp
October 27, 1980

Polymer Collapse Transitions
Institute of Polymer Chemistry, Zabrze, Poland
I. C. Sanchez
October 27, 1980

Dielectric Properties of Polyvinylidene Fluoride--Low Field and High Field Phenomena and Time Effects
Conference on Electrical Insulation and Dielectric Phenomena, Boston, Massachusetts
M. G. Broadhurst, G. T. Davis, and A. S. DeReggi
October 28, 1980

Equation of State Theory of Polymer Blends
Center of Molecular and Macromolecular Studies, Lodz, Poland
I. C. Sanchez
October 28, 1980

Polymer Configurations and Boundaries
NBS Center for Applied Mathematics Colloquium on Mathematical Modeling in Science and Engineering, Gaithersburg, Maryland
R. J. Rubin
October 29, 1980

Polymer Collapse Transitions
Institute of Fundamental Technological Research, Warsaw, Poland
I. C. Sanchez
October 30, 1980

Materials for Removable Prosthodontics
Veterans Administration Hospital, Washington, D.C.
N. W. Rupp
November 6, 1980

New Techniques for the Thermal Analytical Investigation of Polymer Degradation Kinetics
New Polymers and New Applications Symposium, Pittsburgh, Pennsylvania
J. H. Flynn
November 13, 1980

Current Concepts in Meta-Porcelain Systems
University of Texas, San Antonio, Texas
R. W. Hinman and J. A. Tesk
November 14, 1980

Strain Energy Functions of the Valanis-Landel Type
Jet Propulsion Laboratory, Pasadena, California
E. A. Kearsley
November 17, 1980

Analysis of Thermogravimetric Kinetics--Overcoming Complications of Thermal History
Symposium on Thermal Analysis in Polymer Characterization, New York, New York
J. H. Flynn
November 20, 1980

New Developments in Amalgam and Composites
Montgomery County Study Club, Gaithersburg, Maryland
N. W. Rupp
November 20, 1980

Applications of High Resolution Solid-State ^{13}C NMR in Polymers
Allied Chemical Corporation, Morristown, New Jersey
D. L. VanderHart
November 20, 1980

Expectations for Resolution in Solid-State ^{13}C NMR of Polymers
Bell Laboratories, Murray Hill, New Jersey
D. L. VanderHart
November 21, 1980

Equation of State Theories of Polymer Blends
University of Texas, Austin, Texas
I. C. Sanchez
November 25, 1980

Selection and Use of Dental Materials
Southern Maryland Dental Society, Silver Spring, Maryland
N. W. Rupp
December 1, 1980

Physical Testing of Polymers for Use in Circulatory Assist Devices
Fourth Annual Contractors Meeting, Bethesda, Maryland
R. W. Penn
December 3, 1980

Theory of Interfacial Tension in Polymer Mixtures
McGill University, Montreal, Canada
I. C. Sanchez
December 4, 1980

Resolution in Solid-State ^{13}C NMR of Polymers
Monsanto Chemical Company, St. Louis, Missouri
D. L. VanderHart
December 8, 1980

Current Concepts in Dental Research
Georgetown University, Washington, D.C.
J. M. Cassel
January 7, 1981

Prosthodontic Materials: Selection and Use of Amalgam and Composites
Temple University, Philadelphia, Pennsylvania
N. W. Rupp
January 7, 1981

Basis of Piezoelectricity and Pyroelectricity in Polymers
Symposium on Electroactive Polymers and Special Topics, Washington, D.C.
M. G. Broadhurst
January 9, 1981

Field Induced Phase Transitions of Polyvinylidene Fluoride
Gordon Research Conference, Ventura, California
M. G. Broadhurst
January 12, 1981

Materials for Indirect Restorative Dentistry
Navy Dental School, Bethesda, Maryland
N. W. Rupp
January 12, 1981

Dynamic Light Scattering From Dilute Polymer Solutions
University of California, Los Angeles, California
C. C. Han
January 14, 1981

A Computer-Controlled Manometric Permeation Measuring: Hardware and Software Considerations
Washington Area MINC Users Group, Washington, D.C.
J. D. Barnes
January 15, 1981

Loading Rate and Temperature Effects in the Failure of Adhesives and Composites
Seventh SAMPE Symposium on Advanced Composites, Palo Alto, California
D. L. Hunston
January 16, 1981

Dynamic Light Scattering From Dilute Polymer Solutions in the Non-Asymptotic q-Region
University of Washington, Seattle, Washington
C. C. Han
January 19, 1981

Porcelain-to-Metal Restoration and Impression and Die Materials
D.C. Progress Study Club, Washington, D.C.
N. W. Rupp
January 26, 1981

Wear of Dental Composites
U.S. Public Health Service Hospital Seminar, San Francisco, California
W. L. Wu
January 26, 1981

Manipulation of Dental Materials
Veterans Administration Hospital, Washington, D.C.
N. W. Rupp
February 5, 1981

Transport of Radon in Porous Materials
Lawrence Berkeley Laboratory, Berkeley, California
R. J. Rubin
February 11, 1981

Developments in Composite Resins
Academy of Operative Dentistry Annual Scientific Session, Chicago, Illinois
R. L. Bowen
February 12, 1981

Selection and Use of Dental Materials
Barksdale Air Force Base, Shreveport, Louisiana
N. W. Rupp
February 24, 1981

Cutting Tooth Tissues, Pulp Protection, and Microleakage
Georgetown University Dental School, Washington, D.C.
N. W. Rupp
February 26, 1981

The Morphology of Uncrosslinked Polyethylene
Workshop on the Morphology of Polyethylene Power Cable Insulation, Gaithersburg, Maryland
F. A. Khoury
March 3, 1981

Dynamic Light Scattering of Polymer Solutions in the Non-Asymptotic q-Region
State University of New York, Stony Brook, New York
C. C. Han
March 6, 1981

Brownian Motion, Polymer Adsorption, and Steady-State Enzyme Kinetics
California Institute of Technology, Pasadena, California
R. J. Rubin
March 10, 1981

Selection and Use of Dental Materials
Sheppard Air Force Base, Wichita Falls, Texas
N. W. Rupp
March 10, 1981

Failure Behavior of Polymeric Materials
Ecole Polytechnique de Montreal, Montreal, Canada
G. B. McKenna
March 12, 1981

Selection of Prosthodontic Materials
Georgetown University Dental School, Washington, D.C.
N. W. Rupp
March 12, 1981

Brownian Motion, Polymer Adsorption, and Steady-State Enzyme Kinetics
Stanford University, Palo Alto, California
R. J. Rubin
March 13, 1981

Factors Influencing Selection of Fixed Partial Denture Alloys, Part I
Annual Meeting of the American Association of Dental Schools, Chicago, Illinois
R. W. Hinman
March 15, 1981

Deformation and Failure Behavior of Ultra High Molecular Weight Polyethylene
University of Toronto, Toronto, Canada
G. B. McKenna
March 16, 1981

Mechanical Durability of Candidate Elastomers for Blood Pump Applications
Toronto Division of the Canadian Society for Biomaterials, Toronto, Canada
G. B. McKenna
March 16, 1981

Polymer/Polymer Interactions in the Dilute Regime
American Physical Society, Phoenix, Arizona
I. C. Sanchez
March 16, 1981

Adsorption of Benzoic Acid on Hydroxyapatite: Effect of Solvent and Hydrogen Bonding
International Association for Dental Research, Chicago, Illinois
D. N. Misra
March 19, 1981

A Planar Ca-PO_4 Sheet Structure: $CaBrH_2PO_4 \cdot 4H_2O$
International Association for Dental Research, Chicago, Illinois
S. Takagi
March 20, 1981

Copper-Free Amalgams: Dimensional Changes After 4.5 Years
International Association for Dental Research, Chicago, Illinois
G. C. Paffenbarger
March 21, 1981

Selection of Materials and Handling to Prevent Microleakage
Georgetown University Dental School, Washington, D.C.
N. W. Rupp
March 26, 1981

Some Aspects of the BKZ Elastic Fluid Theory
Catholic University, Washington, D.C.
L. J. Zapas
March 26, 1981

Dental Amalgam
U.S. Navy Dental Center, Bethesda, Maryland
N. W. Rupp
March 30, 1981

Indirect Restorative Materials
Veterans Administration Hospital, Washington, D.C.
N. W. Rupp
March 30, 1981

Current Status of the Ceramometal Restoration
National Naval Medical Center, Bethesda, Maryland
R. W. Hinman
April 1, 1981

Diffusion and Transport in Polymers
University of North Carolina, Raleigh, North Carolina
L. E. Smith
April 1, 1981

Thermogravimetric Analysis Kinetics
Symposium on Instrumental and Physical Characterization of Macromolecules of the Macromolecular Secretariat, Atlanta, Georgia
J. H. Flynn
April 2, 1981

The Selection of Composite Restorative Materials and Their Proper Use
Georgetown University Dental School, Washington, D.C.
N. W. Rupp
April 2, 1981

The National Cost of Corrosion and How its Magnitude is Measured
National Research Center, Cairo, Egypt
E. Passaglia
April 5, 1981

The Selection and Use of Dental Materials
St. Louis Dental Society, St. Louis, Missouri
N. W. Rupp
April 6, 1981

Effects of Excluded Volume and Pre-Averaging Oseen Tensor for Dilute Polymer Solutions by Dynamic Light Scattering
University of Michigan, Ann Arbor, Michigan
C. C. Han
April 7, 1981

Mechanical Properties and Orientation in Polymers
University of Leeds, Leeds, England
A. Peterlin
April 7, 1981

Fracture Mechanics and Fracture Control Design
American University, Cairo, Egypt
E. Passaglia
April 8, 1981

Measuring Elastic Strain Energies
Catholic University, Washington, D.C.
E. A. Kearsley
April 9, 1981

Review of NBS and NRL Programs on Adhesion
Navy, Army, Air Force, and NASA Workshop on Adhesion, Dayton, Ohio
D. L. Hunston
April 24, 1981

Materials Used in Dental Health Therapy
University of Virginia, Charlottesville, Virginia
G. C. Paffenbarger
April 27, 1981

Electrical Behavior of PVDF
Workshop on High Energy Density Capacitors, Maxwell Laboratories, San Diego, California
M. G. Broadhurst
April 28, 1981

Materials for the Laboratory Technician
Veterans Administration Hospital, Washington, D.C.
N. W. Rupp
April 28, 1981

Composites and Amalgams
Mid-Oregon Study Club, Bend, Oregon
N. W. Rupp
May 1, 1981

Selection and Use of Dental Materials for the General Dentist
Oregon Study Club, McMinnville, Oregon
N. W. Rupp
May 4, 1981

Compatibility of Dental Porcelains and Alloys
Johnson and Johnson Research Laboratories, East Windsor, New Jersey
J. A. Tesk
May 11, 1981

Kinetics of Polymer Degradation
Polytechnic Institute of New York, Brooklyn, New York
J. H. Flynn
May 13, 1981

Elastic Strain Energy Functions
Illinois Institute of Technology, Chicago, Illinois
E. A. Kearsley
May 14, 1981

Selection and Use of Dental Materials
Offutt Air Force Base, Omaha, Nebraska
N. W. Rupp
May 20, 1981

Models for the Diffusion in Polyolefins
New York Academy of Sciences, New York, New York
L. E. Smith
May 27, 1981

The Use of "Toughened" Polymers in Structural Adhesives and Composites
Martin Marietta Laboratories, Baltimore, Maryland
D. L. Hunston and J. L. Rushford
May 29, 1981

General Rheology and its Applications in Adhesion
Workshop on Adhesion and Adhesives, Kent State University, Kent, Ohio
D. L. Hunston
June 8, 1981

Random Walks on Lattices: The Problem of Visits to a Set of Points Revisited
Twente University of Technology, Enschede, Netherlands
R. J. Rubin
June 17, 1981

Fluid Flow Problems and the Use of Polymeric Additives
Workshop on Applied Rheology for the Inudstrial Chemist, Kent State University, Kent, Ohio
D. L. Hunston and R. Y. Ting
June 18, 1981

Fracture Behavior of Brittle Materials
Workshop on Applied Rheology for Industrial Chemists, Kent State University, Kent, Ohio
D. L. Hunston
June 19, 1981

Application of Factor Jump Thermogravimetry to Polymer Degradation Studies
Eleventh Annual Summer Institute in Polymer Science and Technology, New Paltz, New York
B. Dickens
June 23, 1981

Solution Oxidation Studies With Styrene Polymers
Eleventh Annual Summer Institute in Polymer Science and Technology, New Paltz, New York
B. Dickens
June 23, 1981

Effect of Solution Surfaces on Polymer Configurations
University of Groningen, Groningen, Netherlands
R. J. Rubin
June 24, 1981

Equation of State Theories of Low and High Molecular Weight Liquid Mixtures
Exxon Corporate Research Laboratories, Linden, New Jersey
I. C. Sanchez
July 7, 1981

Small Angle Neutron Scattering on Elastomer Networks
Gordon Research Conference, New London, New Hampshire
C. C. Han
July 14, 1981

^{13}C NMR in Oriented Polymeric Solids
Twenty-Third Rocky Mountain Conference for Applied Spectroscopy, Denver, Colorado
D. L. VanderHart
August 3, 1981

Surface Thermodynamics of Liquid Polymers: Theory
International Symposium on Physicochemical Aspects of Polymer Surfaces, New York, New York
I. C. Sanchez
August 23, 1981

Effect of Matrix Toughness on Interlaminar Fracture of Composites
W. D. Bascom and D. L. Hunston
American Chemical Society, New York, New York
August 24, 1981

Fracture Toughness of the Polymers Used in Adhesive Bonding and Composites
D. L. Hunston, J. L. Rushford, J. L. Bitner, W. D. Bascom, and R. J. Moretton
American Chemical Society, New York, New York
August 24, 1981

Inferences About Molecular Motion From Proton-Decoupled ^{13}C NMR Spectra of Polymers
American Chemical Society, New York, New York
D. L. VanderHart
August 25, 1981

Pressure as an Important Variable in Thermogravimetric Studies of Polymer Degradations
Second European Symposium on Thermal Analysis, Aberdeen, Scotland
B. Dickens
September 2, 1981

Role of Thermal Analysis in the Lifetime Prediction of Polymers
Second European Symposium on Thermal Analysis, Aberdeen, Scotland
J. H. Flynn
September 3, 1981

Mettler Award Address
Royal Society of Chemistry, Salford, England
J. H. Flynn
September 7, 1981

Thermal Degradation of Polyethylene and Polypropylene, Studied Using Thermogravimetry
International Workshop in Thermal Analysis, Salford, England
B. Dickens
September 8, 1981

Dr. Fusayama's Books on Some New Departures in Operative Dentistry
American College of Dentists, New York, New York
G. C. Paffenbarger
September 9, 1981

Seminars for Staff and Guests

The Chemistry and Structure of Guayule Rubber
Donald McIntyre
University of Akron, Akron, Ohio
June 3, 1980

Consideration of Some Factors Influencing Compatibility of Dental Porcelains and Alloys
John A. Tesk
National Bureau of Standards, Washington, D.C.
June 30, 1980

Electron Beam Probing of Charge Distributions in Polymer Films
David W. Tong
General Electric Company, Schenectady, New York
July 10, 1980

Dielectric Behavior of Vinylidene Fluoride-Tetrafluoroethylene Copolymers
Naokazu Koizumi
Kyoto University, Kyoto, Japan
September 3, 1980

Simulation of Polymer Dynamics
Marshall Fixman
Colorado State University, Fort Collins, Colorado
October 6, 1980

Non-Linear Viscoelasticity of Polymers and the Fracture Behavior by Finite Element Analysis
Shiro Matsuoka
Bell Laboratories, Murray Hill, New Jersey
October 6, 1980

Chemical Kinetics in the Hydrolytic Degradation of Polyester Based Polyurethanes
Daniel W. Brown
National Bureau of Standards, Washington, D.C.
October 8, 1980

High Modulus/High Strength Organic Fibers: Spinning and Mechanical Properties
W. Bruce Black
Monsanto Textiles Company, Pensacola, Florida
October 29, 1980

Influence of Internal Structure on Small Deformation Properties of Crystalline Polymers
James Sefaris
University of Washington, Seattle, Washington
October 29, 1980

The Role of Chemical Bonding in the Adhesion of Polymers
Alan N. Gent
University of Akron, Akron, Ohio
October 31, 1980

Crystallization Kinetics of cis Polyisoprene at High Pressures
Eddy N. Dalal
University of Utah, Salt Lake City, Utah
November 6, 1980

Healing of the Polymer-Polymer Interface by Reptational Motion
Stephen Prager
University of Minnesota, Minneapolis, Minnesota
November 7, 1980

Frequency Dependence of Remanent Polarization and the Correlation of Piezoelectric Coefficients With Remanant Polarization in PVDF
J. Charles Hicks
Naval Ocean Systems Center, San Diego, California
November 10, 1980

FTIR Characterization of Conformational Changes in Amorphous Poly(Ethylene Terephthalate) During Volume Recovery
Robert S. Moore
Eastman Kodak Company, Rochester, New York
November 13, 1980

Light and Neutron Scattering Studies of Concentrated Polymer Solutions
Jeffrey T. Koberstein
Princeton University, Princeton, New Jersey
November 14, 1980

New Substituted Polyethers and Polysulfides via Ring Opening Polymerization
David Tirrell
Carnegie-Mellon University, Pittsburgh, Pennsylvania
November 17, 1980

Fracture Mechanics of Plastic Products
Michael D. Taylor
Manchester Polytechnic, Manchester, England
November 18, 1980

Polymer Compatibility and Phase Transitions
Ludwik Leibler
Centre de Recherches sur les Macromolecules, Strasbourg, France
November 21, 1980

Fluid Phase Equilibria
Jean-Louis Guillevic
Ecole Nationale Superieure des Mines de Paris, Paris, France
November 24, 1980

Dependence of Crystalline Morphology of Polyethylene Fractions on Molecular Weight and Crystallization Temperature
Ingrid Voigt-Martin
Johannes-Gutenberg-Universität, Mainz, West Germany
November 25, 1980

Fluorescence Studies of Polymer Conformation and Chain Dynamics
Mitchell A. Winnik
University of Toronto, Toronto, Canada
December 11, 1980

Applications of Finite Element Modeling in Dentistry
Otto Widera
University of Illinois, Chicago, Illinois
December 15, 1980

Irreversible Deformation Processes in Amorphous Polymers
Eric Baer
Case Western Reserve University, Cleveland, Ohio
December 30, 1980

Reversible Crystallization and the Thermodynamics of Piezoelectricity in PVDF
Philip L. Taylor
Case Western Reserve University, Cleveland, Ohio
January 8, 1981

Some Artifacts and Experimental Constraints in SANS Studies of Polymers
George D. Wignall
Oak Ridge National Laboratory, Oak Ridge, Tennessee
January 26, 1981

Structural Aspects of Segmented Polyurethanes and Correlations With Mechanical Behavior
Garth Wilkes
Virginia Polytechnic Institute and State University, Blacksburg, Virginia
January 29, 1981

Miscible Polymer Blends
Donald Paul
University of Texas, Austin, Texas
February 6, 1981

The Role of Mechanical Stress in Polymer Networks in Equilibrium and in Transport
Alexander Silberberg
Weizmann Institute of Science, Rehovot, Israel
February 26, 1981

Block Copolymers as Surfactants Between Immiscible Solvents
Robert Cantor
College de France, Paris, France
March 3, 1981

Global and Local Structure Function in a Self-Repelling Chain Polymer
Thomas Witten
University of Michigan, Ann Arbor, Michigan
March 5, 1981

Composite Restorative Materials
Robert Denyer
Imperial Chemical Industries, Ltd., Macclesfield, England
March 23, 1981

Viscosity of Semi-Dilute Polymer Solutions
Mireille Adam
CEN de Saclay, Gif-sur-Yvette, France
March 25, 1981

New Aspects of the Microhardness of Polyethylene Relating to Texture and Morphology
Francisco Baltá Calleja
Instituto de Estructura de la Materia, Serrano, Spain
March 26, 1981

Phase Transition and Morphology in PVDF
B. Servet
Thomson-CSF, Orsay, France
March 26, 1981

Molecular Orientation and Chain Relaxation in Polystyrene Stretched Above Tg
Lucien Monnerie
Ecole Superieure de Physique de Chimie Industrielles de Paris, Paris, France
March 27, 1981

High Pressure Phase Equilibria of Polyethylene/Ethylene Mixtures
Dominic Richon
Ecole Nationale Superieure des Mines, Paris, France
March 27, 1981

The Morphology of Polyethylene Crystallized Under the Influence of Flow
David Grubb
Cornell University, Ithaca, New York
March 30, 1981

Fundamental Processes in the Photo-Oxidation of Polyolefins
James Guillet
Lash Miller Chemical Laboratories, Toronto, Canada
March 30, 1981

The Structure of Aromatic Polyesters
Ivan H. Hall
Purdue University, West Lafayette, Indiana
March 30, 1981

The Diffusion of Linear, Branched, and Cyclic Polymers in Concentrated Solutions and Melts of a Linear Polymer
Jacob Klein
University of Cambridge, Cambridge, England
April 3, 1981

Orientational Distribution and Molecular Motion in Oriented Deuterated Polyethylene From ^{2}H-NMR Experiments
Hans Sillescu
University of Mainz, Mainz, West Germany
April 3, 1981

Recent Developments in Vibrational Spectroscopy of Polymethylene Molecules
Guiseppe Zerbi
Institute of Macromolecular Chemistry, Milan, Italy
April 9, 1981

Phase Behavior of Polystyrene (I) Poly(2,6-Dimethyl-1,4-Phenylene Oxide) (II) and Their Brominated Derivatives
Roger P. Kambour
General Electric Company, Schenectady, New York
April 17, 1981

Morphological and Mechanical Studies of Oriented Block Copolymers by SAXS, SANS, and EM
Georges Hadziioannou
University of Massachusetts, Amherst, Massachusetts
April 22, 1981

NMR Spatial Mapping for Medical Applications and Nondestructive Evaluation
Jerome I. Kaplan
Indiana University, Indianapolis, Indiana
April 23, 1981

Ion Distribution Around a Polyelectrolyte by the Monte Carlo Method
Bruno H. Zimm
University of California, San Diego, California
April 29, 1981

Micromechanics, Microstructure, and Fracture of Crazes
Edward J. Kraemer
Cornell University, Ithaca, New York
May 1, 1981

Mechanical Properties of Polymer Liquid Crystals
Masao Horio
Kyoto University, Kyoto, Japan
May 15, 1981

The Physical Properties of Acrylic Blends
Robert Kusy
University of North Carolina, Chapel Hill, North Carolina
May 27, 1981

On the Optical and Mechanical Behavior of Viscoelastic Fluids in Shear
Bernard D. Coleman
Carnegie-Mellon University, Pittsburgh, Pennsylvania
June 3, 1981

Rheology of Rod-Like Liquid Crystal Polymers
Kurt Wissbrun
Celanese Research, Summit, New Jersey
June 8, 1981

Crystal Structure of a "Simple" Polymer PVF_2
Jerome B. Lando
Case Western Reserve University, Cleveland, Ohio
June 9, 1981

Structure Determination of Crosspolymerized Poly(1,11-Dodecadiyne)
Jerome B. Lando
Case Western Reserve University, Cleveland, Ohio
June 9, 1981

Light Scattering and Electro-Optics of Biomembrane
Hyuk Yu
University of Wisconsin, Madison, Wisconsin
June 12, 1981

The Feasibility of Screen Film Combinations in Intra-Oral Dental Radiography
Tomohero Okano
National Institute for Dental Research, Bethesda, Maryland
June 16, 1981

Activities of the Australian Dental Standards Laboratory and Research on Bonding to Teeth
Derrick Beech
Australian Dental Standards Laboratory, Victoria, Australia
June 17, 1981

Relaxation of Stresses in Crazes at Cracked Tips and Rate of Craze Extension
Elio Passaglia
National Bureau of Standards, Washington, D.C.
June 18, 1981

Motion of Spheres in Polymer Solutions
Carlos Tiu
Auburn University, Auburn, Alabama
July 6, 1981

"Absolute" Crosslink Density Determinations
Emory Menefee
U.S. Dept. of Agriculture, Berkeley, California
July 7, 1981

Applications of Finite Element Modeling in Dentistry
Otto Widera
University of Illinois, Chicago, Illinois
July 7, 1981

Behavior of Ferroelectric Ceramics and PVF_2 Polymers Under Shock Loading
Francois Bauer
Institut Franco-Allemand de Recherches de Saint-Louis, Saint-Louis, France
July 8, 1981

Molecular Weight Distribution From Stretch Relaxation: A New Algorithm for Relaxation Distribution
Emory Menefee
U.S. Dept. of Agriculture, Berkeley, California
July 8, 1981

NMR Study of Dissolution of Highly Insoluble Polysaccharides, Cellulose and Chitin
Marc Vincendon
Centre D'Etudes Nucleaires de Grenoble, Grenoble, France
July 10, 1981

A Visit of Research Institutes and Universities in Four Chinese Cities and Sightseeing to Sites Less-Frequented by Tourists"
Shu-Sing Chang
National Bureau of Standards, Washington, D.C.
July 14, 1981

Integral Equation Method for the Evaluation of the Entropy of Polymer Chains Confined to Very Narrow Cylinders--Application to the Intermediate Phase of Polyethylene
Richard Priest
Naval Research Laboratory, Washington, D.C.
July 24, 1981

The Lowest Excited Electronic State in Trans-Polyacetylene
Eugene A. Imhoff
Cornell University, Ithaca, New York
August 4, 1981

Structure and Morphology of Nascent Polyethylene Obtained by Ziegler-Natta Catalysts
Antonio Munoz-Escalona
Ministerio de Sanidad y Asistencia Social, Caracas, Venezuela
September 14, 1981

Technical and Professional Committee Participation and Leadership

Academy of Operative Dentistry
N. W. Rupp
Councilor

American Academy of Gold Foil Operators
N. W. Rupp
Councilor

American Association of Dental Research/International Association of Dental Research
G. M. Brauer
Session Chairman

W. E. Brown
Member: Biological Mineralization Research Award Committee
Mineralized Tissue Group, Chairman
Mineralized Tissue Group, Councilor

J. M. Cassel
Washington Section Delegate

J. A. Tesk
Member: Dental Materials Group
Executive Committee

American Chemical Society
J. M. Antonucci
Member: Board of Managers
Calendar Editor for Capital Chemists

G. M. Brauer
Member: Meetings and Expositions Committee
Special Events Committee, Chairman

American College of Dentists
N. W. Rupp
Member: Award Committee re Robert J. Nelsen, Chairman

American Dental Association Acceptance Program
J. A. Tesk
Member: Porcelain Metal Systems

American Institute of Mining, Metallurgical, and Petroleum Engineers
R. M. Waterstrat
Member: Committee on Alloy Phases

American Institute of Physics
R. K. Eby
Chapter Editor, 1981 Physics Handbook

E. A. Kearsley
Member: Committee for Public Policy

American National Standards Institute
MD156: Dental Materials and Devices
R. L. Bowen
Member: Toxicity Tests, Secretary

G. M. Brauer
Member: Denture Resins, Chairman

J. M. Cassel
Member: C054: Medical Devices Standards Management Board, Executive Committee

N. W. Rupp
Member: Alloy for Dental Amalgams, Chairman
Amalgamators for Dental Amalgams, Chairman
Dispensers for Mercury and Alloys for Dental Amalgams, Chairman
Mercury for Amalgams, Chairman
Pit and Fissure Sealants
Restorative Materials Group, Chairman

J. A. Tesk
Member: Base Metal Alloys
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Ferroelectrics Journal
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Macromolecules (in press)

On the Dynamic Structure Factor, $S(q,\omega)$ of Polymers in Dilute Solution
C. C. Han and A. Z. Akcasu
Polymer (in press)

A Basis for Predicting Long-Time Behavior From Short-Time Tests of Geothermal Sealants
E. A. Kearsley
Geothermal Seals, ASTM (in press)

Effects of Poling Field and Time on Pyroelectric Coefficient and Polarization Uniformity in Polyvinyl Fluoride
S. B. Lang, A. S. DeReggi, and M. G. Broadhurst
Ferroelectrics (in press)

New Struvite Analogue, $MgNaPO_4 \cdot 7H_2O$
M. Mathew, P. Kingsbury, S. Takagi, and W. E. Brown
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Configurational Properties of Comb-Branched Polymers
F. L. McCrackin and J. Mazur
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Cyclic Loading of Carbon Black Filled Butyl Rubber
G. B. McKenna and L. J. Zapas
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Random Walks on Lattices. The Problem of Visits to a Set of Points Revisited
R. J. Rubin and G. H. Weiss
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Application of Photon Correlation Spectroscopy
D. Schaefer and C. C. Han
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Water Rich Hydrates. The Crystal Structure of $Mg_2KH(AsO_4)_2 \cdot 15H_2O$ and $Mg_2KH(PO_4)_2 \cdot 15H_2O$
S. Takagi, W. E. Brown, and M. Mathew
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Physical Metallurgy of Dental Casting Alloys
J. A. Tesk and R. M. Waterstrat
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Influence of Molecular Packing on Solid-State ^{13}C Chemical Shifts: The n-Alkanes
D. L. VanderHart
J. Magn. Reson. (in press)

Resolution in ^{13}C NMR of Organic Solids Using High Power Proton Decoupling and Magic Angle Sample Spinning
D. L. VanderHart, W. L. Earl, and A. N. Garroway
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Analysis of Selected Alloys in the Systems Cr-Pd, Cr-Ru, V-Pd, and Ta-Pt
R. M. Waterstrat
J. Less-Common Metals (in press)

The Crystal Structure of the Low Temperature Phase (II) of Polytetrafluoroethylene
J. J. Weeks, E. S. Clark, and R. K. Eby
Polymer (in press)

Disorder in the Crystal Structures of Phases I and II of Copolymers of Tetrafluoroethylene and Hexafluoropropylene
J. J. Weeks, R. K. Eby, and E. S. Clark
Polymer (in press)

Representation of Long-Time Creep in a Pure-Gum Rubber Vulcanizate
L. A. Wood
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Effect of Polymer Molecular Variables on Drag Reduction
J. L. Zakin and D. L. Hunston
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Special Publication

Binary Phase Diagrams of Transition Elements
R. M. Waterstrat
NBS Special Publication 564 (May 1980)

Patents

Composite Dental Material
R. L. Bowen
July 29, 1980
U.S. Patent 4,215,933

Tertiary Aromatic Amine Accelerators in Acrylic Resin
H. Argentar
January 6, 1981
U.S. Patent 4,243,763

Non-Polymerization Inhibiting, High Strength Dental Cements, Restoratives and Adhesive Based on Vanillic Acid Esters, Carboxylic Acids and Zinc Oxide
G. M. Brauer, J. W. Stansbury, and H. Argentar
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Use of Polyfunctional Surface-Active Comonomers and Other Agents to Improve Adhesion Between a Resin or Composite Material and a Substrate
R. L. Bowen
February 17, 1981
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R. M. Waterstrat
Filed April 1981

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R. L. Bowen
Filed May 1981

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C. K. Chiang
Filed May 1981

Workshop

Morphological Studies of Power Cable Insulation Failure
Electric Power Research Institute, Gaithersburg, Maryland
M. G. Broadhurst
May 1981

External Recognition

1981 Hollenback Memorial Prize
Academy of Operative Dentistry
February 1981
R. L. Bowen

1980 Mettler Award in Thermal Analysis
North American Thermal Analysis Society
October 1980
J. H. Flynn

Fellow
North American Thermal Analysis Society
October 1980
J. H. Flynn

METALLURGY DIVISION

METALLURGY DIVISION (564)

R. Mehrabian, Chief
A. C. Fraker, Deputy Chief
D. M. G. Summers, Secretary

The mission of the Metallurgy Division is to provide data, measurement methods, standards and reference materials, concepts, and information on the fundamental aspects of processing, structure, physical properties, and performance of metals and alloys to industry, Government agencies, and scientific organizations.

The program of the Division involves studies of metals and alloys in order to foster their safe, efficient, and economical utilization to meet our national needs within the larger framework of the materials cycle. Competences are developed and maintained in the general areas of chemical metallurgy with special emphasis on phase diagrams and phase stability; process metallurgy; quantitative microstructural characterization including nondestructive evaluation; properties including friction, wear and the application of metals as synthetic orthopedic implants. The Division also makes a significant contribution as a national resource of metallurgical information through its Diffusion Data Center and Alloy Phase Diagram Data Center. It provides consultation and assistance to other Government agencies and standards organizations in the development of necessary test methods and standards. The programs of the Metallurgy Division are designed to help us meet our future national needs for materials, which will depend in large measure on our response to forces which are now well recognized. Some of these are classical laws of supply and demand; others include such national problems as energy, environment, productivity, and such international problems as assured availability of materials from overseas sources.

For example, our Division, in addition to being involved in theoretical and experimental studies of phase stability, has a joint effort with the American Society for Metals to provide critically evaluated phase diagrams to the metallurgical community. The American Society for Metals is presently getting a $4 million commitment from the metals producer and user industries for their contribution to this program. Advancement in the understanding of phase diagrams and the development of predictive models for phase stability are essential in the development of new alloys for our future needs. These could include stronger and lighter alloys for the transportation industry to reduce energy cost, new alloys specifically designed to exploit the beneficial effects of innovative new processes such as those referred to as rapid solidification processes, and alloys which would permit substitution for scarce or unavailable elemental constituents.

The detailed, programmatic content of the Division that follows is described in the four general task areas. The four tasks in the Metallurgy Division are specifically related to two programmatic initiatives, a competence initiative, and a major agreement on phase diagrams between the American Society for Metals and NBS:

Task 12142--STRUCTURE CHARACTERIZATION

This task addresses the Synchrotron Competence Initiative, the application of NDE (acoustic emission and ultrasonics) to materials characterization, and the activities on analytical electron microscopy.

Task 12143--METALLURGICAL PROCESSING

This task contains all of the present competences in metals processing (e.g., rapid solidification, surface modification, etc.) and is the foundation for the Productivity Increase in Metals Processing Initiative in the FY82 budget. The Diffusion in Metals Data Center is located in this task.

Task 12144--MECHANICAL PROPERTIES AND WEAR

This recently expanded task contains all the wear activities initiated in the FY80 Durability Initiative. It also contains the research activities on the use of metals as synthetic implants.

Task 12145--CHEMICAL METALLURGY

The Alloy Phase Diagram Data Center is in this task. The joint American Society for Metals/NBS cooperative agreement utilizes the resources of this task to develop and disseminate critically evaluated phase diagrams, and on-line computer graphics systems coupled to predictive thermodynamic models. The quarterly ASM/NBS Bulletin of Alloy Phase Diagrams is also published under this task.

The technical activities under the various tasks are closely interrelated and address the overall mission of the Division to meet our present and future societal needs for metals. The central purpose of these scientific activities is to probe the relationships among processing conditions, the internal structure of metals, and their properties and performance. The resulting knowledge can be used to efficiently produce, shape, and otherwise process metals to control their properties and achieve the desired reliable and durable performance in the finished product.

Critical data compilations are being developed and delivered to users concerned with alloy properties, diffusion, and phase diagram information. Standard reference materials are being produced for electron microscope calibration, electron microprobe analysis, and electrical conductivity. Contributions are made to NBS programs in nondestructive evaluation, recycled oil and materials, and artifical implants.

Productive interactions with other groups at NBS exist in areas such as surface analysis, wear, microstructural characterization, acoustic emission, and phase diagrams. Computer graphics methods incorporating phase diagram predictive techniques and thermodynamic data are being developed in collaboration with the Applied Mathematics Division of the National Engineering Laboratory.

The results of our metallurgical research are communicated to the scientific community through technical publications, lectures, active participation of Division members on various national and international committees, personal contacts, and the organization and sponsorship of conferences and meetings on various subjects such as acoustic emission, synthetic implants, alloy phase formation, solidification, wear, and mechanical failure prevention. For example, the personnel in the Division serve on numerous ASTM Committees, including Chairman of the B-6 Committee and Past Chairman of Committee E-42, Vice Chairman of Committee G-2, and chairman of several subcommittees. The technical staff have organized and chaired two international conferences on Rapid Solidification Processing, an international conference on Implant Retrieval: Material and Biological Analysis, the 1981 International Conference on Wear, and are organizing the 1982 International Conference on NDE. The Metallurgy Division's staff serve on over sixty other national professional and technical committees.

The Metallurgy Division also acts as coordinator of a variety of industry/academia/Government workshops. It coordinated and co-sponsored with COMAT the 1981 Briefing/Workshop on Rapid Solidification Technology. The aim of this meeting was to first provide the private sector with the Government-wide implementation strategy for rapid solidification technology in the next five years; and second, to seek industry/university input and involvement in order to effect a wider range of applications of this technology-based "breakthrough." The recommendations of this Workshop are now being formalized for distribution to all the Government agencies involved.

The Metallurgy Division's programs also include direct contributions to industry through the NBS Research Associate Program. Extensive interaction with universities exists through the Cooperative Education Program, NBS Postdoctoral Program, and faculty guest workers. Considerable interaction also exists with other Government agencies, standards organizations, and the technical community at large. For example, the Division performs research for the following Government agencies: the National Aeronautics and Space Administration, the Office of Naval Research, the Defense Advanced Research Project Agency, the Department of Energy, the Naval Ship Research and Development Center, and the U.S. Army Materials and Mechanics Research Center.

The available competences in the Division were strengthened and expanded in the past two years by:

- A successful budget initiative in the area of metallic wear.
- A new competence initiative within the National Bureau of Standards to develop research programs at the Synchrotron Light Source at Brookhaven National Laboratory with the main materials expertise to reside within the Metallurgy Division.
- Development of facilities and new programs in metals processing including liquid/solid transformations (e.g., rapid solidification, solidification-segregation) and innovative measurement techniques.
- Development of a vigorous experimental and theoretical program in evaluation and computerization of phase diagrams and coupling of same to industry through an agreement with the American Society for Metals.

A major proposed expansion of the Metallurgy Division's activities in the area of Productivity in Metals Processing is presently in Congress. The aims and objectives of this 1982 budget initiative are to provide industries with data, measurement techniques and predictive models elucidating the interrelationships between metals processing/structure/property and performance.

MICROSTRUCTURE CHARACTERIZATION
Task 12142 and

SYNCHROTRON RADIATION RESEARCH FOR MATERIALS SCIENCE
Task 51105

Innovative processing techniques are being developed to produce significant new microstructures and structural/property relationships. Coupled with increased industrial emphasis on quality control and automation, these require a range of microstructural characterization and nondestructive evaluation methods. The objectives of this task are to address this challenge by the development of measurement methods including nondestructive techniques and standards for the advanced quantitative characterization of metallurgical microstructures. These developments would permit automatic control methods for manufacturing and in-service use of industrial alloys. Methodologies include x-ray, optical and electron microscopy, eddy current, magnetic particles, positron annihilation, acoustic emission, and ultrasonic methods.

A new competence program in Synchrotron Radiation was initiated in FY80 as a part of this task. The availability of intense tunable well-collimated radiation at synchrotron radiation facilities will permit radical gains in experimental and theoretical materials science. As a joint NBS/Naval Research Laboratory (NRL) effort, we aim to establish an x-ray instrumentation complex at the National Synchrotron Light Source and to use it to perform frontier experiments in transformations in materials, kinetics studies, furtherance of x-ray optics, and the study of inner shell dynamics. One intermediate-term goal of this effort is to establish an advanced x-ray analysis capability at Brookhaven and apply this to topographic analysis of cracks in a stressed metal alloy and to glass-crystal metal alloy transitions. FY81 accomplishments in this portion of the task were:

- The design of monochromators and experimental stations for small angle scattering, x-ray topography and inelastic scattering at the National Synchrotron Light Source (NSLS), at Brookhaven.

- The observation of moving magnetic domain walls in the interior of Ni single crystals by real time x-ray topography using synchrotron radiation with x-ray image magnification.

- The establishment of in-house focused EXAFS capability in the reflection and transmission geometries and initial application to the characterization of metallic glass.

- The measurement of residual stress profiles in thick (> 1 cm) structural alloys using 100 to 200 keV x-rays by an energy dispersive method.

Other programmatic goals of this task are to evaluate quantitatively acoustic emission in steels and aluminum alloys and compare with theory, and to develop ultrasonic spectroscopy to the point that it can be used in microstructure characterization and quality control for defects during processing and use of structural alloys. During FY81 new programs were initiated on eddy current standards and coupling nondestructive evaluation with rapid solidification

processing. The better effort includes both microstructure characterization studies through ultrasonic measurements and the monitoring of melting and solidification events during surface modification by AE. Other efforts are aimed at developing new nondestructive evaluation (NDE) methods such as positron annihilation and in placing established techniques such as the magnetic particle method on a more quantitative and reproducible basis. The NML-Scanning Electron Microscopy (SEM) facility is also located in this task. This facility not only serves various on-going research efforts, but also is used in the development of standard reference materials for SEM. Finally, two distinguished visiting scientists were actively involved in the activities of this task during FY81. They were: Dr. M. Rosen of Ben Gurion University, Israel, and John Hopkins University, Maryland, and Dr. H. N. G. Wadley of the A.E.R.E., Harwell, England.

The task is divided into subtasks whose activities and accomplishments over the past year are described next.

Synchrotron Radiation Research for Materials Science
Task 51105, and

Application of Synchrotron Radiation to Materials Science
Subtask 1 of Task 12142

M. Kuriyama, W. J. Boettinger, G. G. Cohen, R. C. Dobbyn, R. D. Spal,
H. E. Burdette

As the Center for Materials Science's (CMS) part of the National Bureau of Standards (NBS)/Naval Research Laboratory (NRL) synchrotron radiation research program at the Brookhaven National Synchrotron Light Source (NSLS), a group in the Metallurgy Division has taken a lead in the construction of hard radiation (0.5 A5A) branch lines for CMS scientists and NRL scientists to make use of unique synchrotron radiation characteristics, such as high flux and tunability, for research problems in materials science. The beam lines include facilities for real time topography, small angle scattering, interface/inelastic scattering spectroscopy, and crystallography. Scientific problems are aimed at advancing materials science by utilizing techniques previously impractical. For example, the high flux in the synchrotron beam makes possible the observation of local phenomena in materials in real time. The energy and momentum resolution can be made extremely good so as to increase the precision in the determination of the atomic coordination and arrangement. Furthermore, the tunability of the radiation for the desired energy band pass enables us to focus on a particular atomic species (elemental tunability) for the precise determination of behavior under the influence of neighboring atoms in different local volumes. The ultimate goal in materials science would be the formation and verification of discrete atomistic theory for rates of phase transformations and structure stability. In approaching this goal, we have placed an emphasis in the initial phase, on the development of dynamic in situ measurement capability to obtain an advanced knowledge in kinetics of microstructural transformations, and investigations of short- and long-range order in various local volumes.

Every research team participating in the use of synchrotron radiation at NSLS has been making every effort to create unique and original beam lines and experimental capabilities. The group in the Metallurgy Division is no exception. To accomplish beam line build-up, four activities must be addressed simultaneously.

These are (1) overall beam line design, (2) new x-ray diffraction configurations including the development of prototype instruments, (3) monochromators/experiments design, and (4) computer control. Our basic philosophy for the CMS experiments is to deliver x-ray monochromatic photons of energies between 5 keV and 30 keV by the simplest method and to create a high degree of energy, momentum, and spatial resolutions primarily through flat crystal diffraction optics. The beam is to be transported through Bε windows (10 to 15 mils thick) in the atmospheric pressure of He. The monochromator boxes (hutches) and experimental hutches have also been designed in the simplest and most versatile form. The design and fabrication have been undertaken in collaboration with NRL materials scientists and NSLS scientists.

Since we have decided to use primarily asymmetric flat crystal optics to prepare x-ray beams for experiments, we must, under activity (2), devise and test new methods to meet the requirements of various planned experiments which will use the new optical techniques. We have tested these prototype x-ray optical configurations using both a 12 kW high intensity rotating anode x-ray source and synchrotron radiation at Cornell University (CHESS). A few examples of this activity are described below.

During the past one and a half years, we constructed hardware, such as a real time topographic/microradiographic system with x-ray magnifier, an extended x-ray absorption fine structure (EXAFS) spectrometer with a bent crystal focusing geometry, a small angle scattering spectrometer with double asymmetric crystal x-ray optics and a tunable microdiffractometer with high pressure cell. These were all tested successfully. The results obtained using a small angle scattering spectrometer were reported last year. The tunable microdiffractometer was tested by other CMS scientists.

In the monochromator/experiment design activity, two monochromators are being constructed. Each monochromator consists of two flat crystals driven by computer control. A cylindrical bent focusing monochromator is also being made. The design of experimental stations (hutches) are now completed so that the standard panels required by NSLS regulation can be used for the assembly.

As all experiments must be remotely controlled, the computer control activity is of great importance. We have worked on software and hardware for detector motion, data collection and processing, and multicrystal alignments which include the control over tilt, azimuth, scattering angle, and sample translations. Two LSI 11/23 computers are tested with necessary modules and microprocessors to control two experiments independently at NSLS beam lines. These capabilities have been demonstrated by successful operation of the in-house EXAFS experiment.

Under this competence program started in FY80, we have added Ronald C. Dobbyn this year to our permanent professional staff. Dr. Simon C. Moss, Professor of Physics, University of Houston, has remained as consultant for this year. Through the U.S./Franco International Cooperative Program of Materials Science, Professor Georges Champier, Professor of Metallurgy, Institut National Polytechnique de Lorraine, Ecoles des Mines de Nancy, France, has joined our group as guest worker. This work using synchrotron/x-ray topography was initiated last year (see 1980 Annual Report) with the participation of an NBS scientist in collaboration with the National Science Foundation. We have maintained close

collaboration with Professor Haydn Chen, Univerity of Illinois, Professor Ronald W. Armstrong, University of Maryland, Professor Robert E. Green, Jr., Johns Hopkins University, Professor Barton Roesslor, Brown University, and Professor Yi-Han Kao and Mr. Allan Goldman, State University of New York (Stony Brook), to perform experiments. Several international collaborations have been maintained and initiated with Professor H. J. Queisser and Dr. W. Hartmann, Max-Planck Institut fur Festkorperforschung, Stuttgart, Germany, Professor G. Hildebrandt, Fritz-Haber Institut der Max-Planck Gesellschaft, Berlin, Germany, and Dr. J. Chikawa, Broadcasting Science Technology Laboratories, NHK, Japan, on the development of real time imaging in x-ray topography.

In addition to the synchrotron radiation beam line activity, we have established an in-house EXAFS experimental capability through our prototype development for the synchrotron radiation program. This capability is unique in the field of EXAFS, features automatic focusing with tunable energies of the incident x-ray beam from 5 keV to 25 keV. This system is completely computer controlled and data are analyzed automatically on site. This new system has stimulated interest among many scientists; we are now performing EXAFS experiments on catalysts, layered thin films, oxides, surfaces of thin films, Ti-compounds, metallic glasses, and biological samples with Dr. D. Peterson, Dow Corning, R. von Wingerden and D. Denley, Shell, W. Gibson, SUNY/Albany, L. Hanson, BNL, K. Liang, EXXON, W. Wagner, Bell Labs, and Y.H. Kao, SUNY/Stony Brook. This in-house EXAFS system has also been used by NBS scientists in other centers in collaboration with us. One of the EXAFS technical activities in our Division is described later.

To summarize the present status in this CMS synchrotron radiation program, we have completed designing beam transport and experimental hutches, have completed designing and started the construction of monochromators. Our prototype experiments for testing new x-ray optical methodology, and our experience using synchrotron radiation at CHESS are being used to develop systems for the NSLS beam lines; the construction of a spectrometer for SAXS station has started; the construction of a NSLS topography system has also started. Some highlights of our technical activities in the CMS synchrotron radiation materials science program are described in more detail as follows.

Development of Real Time Monochromatic Radiation Topography with X-ray Magnification

W. J. Boettinger, H. E. Burdette, R. C. Dobbyn, M. Kuriyama

X-ray topography is a nondestructive technique to image certain types of metallurgical and ceramic microstructure from the surface or through the thickness of samples under Bragg diffraction conditions. Depending on the wavelength of the radiation and/or the perfection of the crystalline samples, the depth of material observed can range between 1 μm and 1 mm.

A portable and remote-controlled topographic and microradiographic system has been designed, constructed, and tested with a synchrotron radiation beam at CHESS-B line. This system employs the principles of asymmetric diffraction for crystal topography and x-ray image magnification [1,2]. It will permit real time observation of microstructural details in materials with high spatial resolution. The system consists of a double crystal monochromator, a sample

stage, a double crystal x-ray magnifier, and an image intensifier. The monochromator uses successive diffraction of Si(111) in a symmetric-asymmetric parallel setting. The asymmetric crystal not only provides a wide (1.5 cm x 2.0 cm) and parallel (1 arc/s) monochromatic (8.0 keV) beam but also allows easy harmonic rejection. This beam is quite satisfactory for obtaining ordinary topographs from sample crystals using nuclear emulsion films. Surface and transmission topographs were obtained with synchrotron radiation under 5 GeV, 10 mA, from a nickel single crystal disc 0.6 mm thick, 2 cm in diameter (figure 1). A particularly interesting accomplishment was the topograph from a Heusler ordered alloy (Cu_2MnAl) single crystal using super lattice diffraction (200). These topographs are indicative of the future application of this system [3]. These topographs were taken with less than one hundredth of the normal exposure time required for ordinary x-ray sources.

The x-ray magnifier employs a pair of asymmetric (m = 20, 40 or 70) Si (111) crystals with perpendicular planes of diffraction (figure 2). To record topographs on a real time basis using the x-ray magnifier and image intensifier, a wide x-ray beam from the monochromator is not needed and, in fact, wastes photons. The placement of the asymmetric crystal in the demagnification mode (as a concentrator) ensures the illumination of only the region of the sample crystal viewed by the x-ray magnifier. In fact, this concentrator cancels the reduction of the beam brightness per unit area caused by one of the crystals in the x-ray magnifier.

The samples consisted of Ni single crystals cut and oriented for (111) symmetric diffraction in the transmission geometry. Sample thicknesses correspond to $\mu t \sim 10$, but the transmitted intensity under diffracting conditions was changed only by a factor of $\sim e^5$. The Bragg diffracted beam ($\underset{\sim}{H}$) was monitored using an ionization chamber while the transmitted or forward diffracted beam ($\underset{\sim}{O}$) was incident on the x-ray magnifier. The magnification factor employed here was 20. The first diffraction magnifies the topographic images in the vertical direction while the second magnifies in the horizontal direction. Estimated flux level after this five crystal arrangement is 10^3 photons/mm^2s. In the magnified image, 1 mm corresponds to 50 μm in the sample crystal (figure 3). The topographic images are detected using a phosphor fiber optically coupled to a four stage first generation image intensifier directly viewed by a vidicon. Video images of moving magnetic domain walls under a varying magnetic field were obtained from Ni single crystals in the anomolous transmission geometry (figure 4) [4].

Other possible applications of this technique to observe the structure of materials as a function of position in the sample and time will be found in the areas of phase transition, plasticity, fracture, and corrosion [5].

[1] W. J. Boettinger, H. E. Burdette, M. Kuriyama, and R. E. Green, Jr., Rev. Sci. Instr. 47, 906-911 (1976).

[2] W. J. Boettinger, H. E. Burdette, and M. Kuriyama, Rev. Sci. Instr. 50 (1), 26-30 (1979).

[3] M. Kuriyama and W. J. Boettinger, Materials Engineering, 93, 32-33 (1981).

[4] W. J. Boettinger, H. E. Burdette, R. C. Dobbyn, and M. Kuriyama, Proc. 2nd Int. Conf. on Synchrotron Radiation Instrumentation (to be published in September 1981).

[5] M. Kuriyama and W. J. Boettinger, Application of Synchrotron Radiation to Materials Science, 1981 Materials Research Society Meeting, Boston, November 16-19, 1981.

EXAFS Study of Metallic Glasses. G. G. Cohen, D. R. Black, M. Kuriyama

To date, most of the characterizations of atomic arrangements in metallic glasses have been made using conventional x-ray diffraction. These measurements provide a statistically averaged structural description, which is then used to test three-dimensional structural models.

In the EXAFS process, the central absorbing atom, as well as the neighboring (backscattering) atoms, play a significant role in the interference event. the structural parameters which can be extracted are: (1) the distances between the absorbing atom and the j^{th} shell atoms, (2) the number of atoms in the j^{th} shell, and (3) the relative static or thermal disorder. Polk [1] proposed a structural model for transition metal--metalloid glasses having ~ 80 at . % metal, based on Bernal's [2] dense random packed structure. In this model, the transition metal would form a dense random packed hard sphere and the metalloid would fill in the large eight- and nine-fold coordinated holes. The model suggests that each metalloid is surrounded by eight to nine metal atoms; that there is no metalloid-metalloid nearest neighbor; and that the metal-metalloid distance will be smaller than the sum of the atomic radii of the atoms involved (tendency toward covalent).

We have begun to study how the models go over to the ternary case of two metals and one metalloid. $Pd_{0.775}Cu_{0.06}Si_{0.165}$ ribbons are being investigated using the K-edges of Cu and Pd. Early results using a Cu-K fluorescence measurement (figure 5) indicate some preferential coordination between the Cu and Si atoms. The way in which the coordination might change as a function of kinetics at temperatures below the crystallization temperature is the subject of further investigation. We also have succeeded in making measurements of transmission EXAFS from Pd (K-edge at 24.36 keV), although, in general, adequate resolution is difficult to achieve for higher Z elements with K-edges above 17 keV. The complexity of the local environment about the metal atom in these glasses will require that the Pd-Pd, Pd-Cu, and Pd-Si pairs be extracted from the Fourier transform through careful computer simulations and curve fitting.

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[2] J. D. Bernal, Nature 185, 68 (1960).

X-Ray Residual Stress Mapping In Industrial Materials by Energy Dispersive Diffractometry
Subtask 2 of Task 12142

M. Kuriyama, W. J. Boettinger, C. J. Bechtoldt

This project is part of the Metallurgy Division's participation in the NBS NDE program. The objective is to develop a nondestructive method of mapping the distribution of residual stresses within industrial materials of considerable thickness. This has been carried out in collaboration with Robert Placious, Radiation Physics Division, Center for Radiation Research.

Improved quality control of industrial materials requires quantitative information concerning the stress distribution near cracks under load and residual stress distributions after different types of cold work and heat treatment. This information enhances our understanding of the crack formation and subsequent

propagation in materials, and leads a way to produce better materials in industry. For monitoring the structural integrity of, weld zones, for example, quantitative information is required for the strain distribution near the weld zone including the heat affected zone as well as the fusion zone. The most accurate current method for the determination of residual stresses uses x-ray Bragg diffractometry from the surface of materials [1]. Although the accuracy is far beyond any other techniques, this technique unfortunately is incapable of detecting stresses in the interior of bulk materials (> 1 mm).

Several years ago, we proposed [2] an entirely different approach to the x-ray evaluation of residual strains (or stresses) although it also uses the principles of x-ray diffraction. This approach uses energy dispersive spectroscopy, where an energy dispersive solid state detector is employed with a well-collimated beam of high energy photons. In energy dispersive spectroscopy, one is concerned with energy spectral profiles and peak positions at different energy values, instead of Bragg angles which play a key role in Bragg diffractometry. These Bragg energy peak positions represent the lattice constants in a local volume, and hence local strains. We proved, using ordinary laboratory x-ray sources and thin materials, that the desired resolution and detectability can be achieved for the determination of residual stresses if this technique is employed simultaneously with a curve fitting technique [3]. This year we have demonstrated a similar capability using an industrial (250 kV) radiographic x-ray source for commercial steel plates up to 3 cm (1.18 in.) thick. The distribution of stress can be mapped across the plates with a well-collimated incident beam and a well defined detector opening.

In this method, well-defined diffraction energy peaks should be obtained at energies of 100 keV or more, so that the penetration of a thick material is possible and the stress within the bulk material can be determined. These peaks should have a Gaussian profile so that the curve fitting technique can be used for the determination of the centroid (or peak) positions with the accuracy increased by a factor of 100 over the resolution limit of solid state detectors. All of these principles have been confirmed previously [3] with thin materials using low energy photons. This year's objective is to confirm these points using high energy photons with thick materials. Figure 6 shows the variation of strains (and, in turn, stresses) across a weld zone measured by this proposed technique in one of the Alaskan pipe lines [4,5]. The material is 14.6 mm thick and has a minimum welded zone 6 mm wide centered at position 0. The statistical error (σvalue) in this measurement is less than 3×10^{-4} in strain and 3000 psi in stress. This indicates the detectability of stress. Reproducibility was also confirmed. In this example the counting statistics were only moderate. With longer counting times or an increased photon flux, the counting statistics can be improved. Using laboratory x-ray sources up to 40 kV, strains of 5×10^{-5} (300 psi) can be easily detected with reliable reproducibility and good counting statistics. Thus, the present demonstration of the expanded capability to higher energy has shown a potentially powerful scientific tool to study and characterize flaws and microstructure with great accuracy; for example, weld zones can be studied across the zones through the depth.

[1] J. B. Cohen, H. Dolle and M. E. James, Proceedings of a Symposium on Accuracy in Powder Diffraction, NBS Special Publ. 567, p. 453 (1980).
[2] M. Kuriyama, W. J. Boettinger, and H. E. Burdette, ASNT National Fall Conference, October, Denver, Colorado, p. 49 (1978).

Doppler-Broadened Positron Annihilation Lineshape for Detection of Defects in Materials

Subtask 3 of Task 12142

R. C. Reno, L. J. Swartzendruber

Positrons that annihilate in a metal produce gamma rays whose energy distributions can be explained in terms of a Doppler shift caused by motion of electrons. When defects are present in the metal, they attract and trap positrons and alter the Doppler shifts. A measurement of Doppler-broadened annihilation lineshapes thus gives information on the defect nature of materials. Both the annihilation process and the method of detection leave the sample intact, so the technique is extremely useful for the nondestructive evaluation of materials.

Doppler-broadened lineshape measurements are performed by placing a positron source in contact with the sample to be studied. Positrons enter the sample, slow down to thermal energies, and then annihilate with electrons. Each annihilation produces two gamma rays with a total energy equal to the rest mass energy of the positron-electron pair (1022 keV). The distribution of energy between the two gamma rays depends upon the electronic and defect structure of the sample, and is measured with a high resolution solid state detector-multichannel analyzer system. A lineshape parameter, S, is defined which is a measurement of the inverse width of the distribution.

The addition of a small number of defects to a metal will cause a significant change in the lineshape parameter, and it is this sensitivity that is used to observe changes in defect concentration and type. We have been using this technique to study two phenomena: precipitation hardening in aluminum alloys and crystallization of amorphous Pd-Cu-Si.

A commercial aluminum alloy (2219) was subjected to two different thermomechanical heat treatments prior to age hardening. Positron S-parameters then were measured as a function of aging time for each treatment (see figure 7). Results indicate that positrons can distinguish between defects surrounding the θ' and θ" precipitates formed in the two sets of samples.

Figure 8 shows S-parameter data for a Pd-Cu-Si alloy heat treated at various temperatures in the amorphous and crystalline region. At the onset of crystallization, the S-parameter first rises slightly and then gradually decreases. Such behavior can be explained in terms of the generation of defects at grain boundaries during crystallization.

Characterization Kinetics Study of Amorphous Pd-Cu-Si by Ultrasonic Measurements

Subtask 4 of Task 12142

M. Rosen, H. N. G. Wadley, R. Mehrabian

Metallic glasses exhibit interesting physical and mechanical properties. A glass is generally not in a state of thermodynamic equilibrium, and therefore, tends to structurally relax and ultimately crystallize into a more stable structure when thermal conditions are appropriate. Changes in bulk density and electronic structure associated with the crystallization process are rather insignificant. Nevertheless, appreciable and in some instances extra-

ordinary, variations in several physical properties were observed. Recently, there has been an increasing interest in the behavior of the elastic properties of metallic glasses in relation with the glass transition and crystallization temperature.

The objective of the present investigation was to study the crystallization kinetics of $Pd_{0.775}Cu_{0.06}Si_{0.165}$ ribbons (about 50 μm in thickness) by means of laser-generated and piezoelectrically detected, ultrasonic waves whereby the extensional wave velocity, and consequently the Young's moduli could be determined as a function of crystallization time. The amorphous-to-crystalline kinetics could thus be determined to a high degree of accuracy.

The inherent difficulty of measuring sound-wave velocities in thin-ribbons was overcome by developing a technique applying the load on the specimen by means of rapid deposition of energy from a single-pulse of a Q-switched Nd:YAG laser. A state of unbalanced compressive thermal stress is produced. The stress gradient propogates along the ribbon in the form of an elastic wave. The piezoelectric crystal, at a distance from the spot where the laser radiation was deposited, detects the local displacement. Thus, the transit time of the propagating wave could be determined accurately by means of a transient-pulse recorder. The complete waveform, stored in a computer has not yet been analyzed since it requires the definition of the theoretical criteria with respect to specimen geometry, conversion of propagation modes, and contribution of the detection sensor.

Results of the present investigation indicate that the transition from the amorphous-to-crystalline state in Pd-Cu-Si is time and temperature dependent, (figure 9). The kinetics was determined at three isothermal-holding temperatures. Therefrom, the activation energy for recrystallization was found to be 55 kcal/mol. From the time dependence of the transformation kinetics an insight was gained into the nucleation and growth mechanisms. Corroborative metallographic evidence was found to be in qualitative agreement with the ultrasonic data, (figure 10), suggesting a linear growth law whereby the crystallization front moves from the free surfaces toward the interior.

The present investigation also has revealed an initial increase of about 7.4 percent in the elastic modulus, out of 40 percent for the complete transition from the amorphous to the crystalline state. It appears that this initial increase can be related to a structural relaxation of the amorphous phase that may precede the crystallization process.

Acoustic Emission for NDE
Subtask 5 of Task 12142

J. A. Simmons, R. B. Clough, H. N. G. Wadley, R. Mehrabian

Acoustic emission (AE) is a relatively new technique for nondestructive testing which relies on the detection of stress waves emitted during the motion of flaws or from other microstructural changes in a material component. It is being used as a nondestructive testing technique for monitoring flaw growth in structures and is also being used for materials studies of rapid phase changes such as martensitic transitions and microcrack nucleation and growth.

At NBS a unique approach is being developed for acoustic emission which has as its objective the reconstruction of the source in terms of its stress drop tensor. This will make accessible quantitative observations on dynamic materials phenomena such as rapid solidification, martensitic phase transitions, microcrack nucleation, and devitrification of glasses.

Because of the tensor nature of the emission source, at least six observation channels are necessary for source reconstruction via signal inversion. With this in mind, a multichannel AE system has been constructed and new experimental methods are being developed to permit us shortly to perform a set of critical experiments which will establish the validity of this approach. A good deal of progress has been made during the past year, and all of the elements needed for these tests are essentially complete and are being debugged. In addition, exploratory work has begun on rapid solidification phenomena which shows promise of some real breakthroughs in studying rapid solidification.

Highlights of these activities include: (1) Application of indentation acoustic emission, the new experimental technique developed here, to A533B pressure vessel steel, where through modification by heat treatment and hydrogen charging, AE activity could be varied over the widest possible limits, from virtually none to that of glass. (2) Construction of the quantitative multichannel AE source characterization system. (3) Experimental simulation of thermoelastic AE sources using an Nd-YAG laser. (4) Exploratory AE studies of rapid solidification using directed high energy sources.

The first two results are part of a continuing EPRI research program. The third was part of a guest worker program with AERE, Harwell, in which Dr. Haydn Wadley took part. The last is part of a new DARPA contract for NDE studies of rapid solidification phenomena.

(1) Indentation AE studies in A533B pressure vessel steel. Previous work with indentation here at NBS showed that it could be used to generate reproducible AE signals in hardened tool steel and that these signals could be linked with incremental crack growth. Our objective in the EPRI program has been to generate reproducible AE in A533B pressure vessel steel. The above techniques were not found to be applicable in this material due to its limited hardness (preventing stresses to increase high enough for crack growth) and high fracture toughness. The approach taken here was that of lowering the fracture toughness through temper embrittlement, which could be assisted by grain coarsening and hydrogen charging. By varying these parameters, it was possible to produce AE over a wide range of activity, from essentially none for the as-received plate, up to emissions comparable in activity to that from glass, which is among the most active emitters. In the hydrogen-charged material, surface and subsurface cracks could be found by sectioning, which varied in size up to about 250 microns, a size small enough compared to the shortest acoustic wavelength of about 1000 microns to enable the source to be considered as a point source for signal analysis. These microcracks often could be associated with inclusions. The tendency for these cracks is to lie either connecting to the surface or at a shallow depth. It is believed that this is promoted by the higher concentration of hydrogen near the surface following hydrogen charging because of the laws of diffusion. It also was possible to produce cracks by hydrogen charging following indentation rather than before, presumably due to the residual stress field of the indentation.

All of these considerations make this technique look promising to produce flaws in plate material of A533B for critical experiments to validate the multichannel AE technique under development here.

(2) Multichannel AE system. As has been discussed above, a multichannel AE system is required for source reconstruction via signal inversion. Such a system has been constructed and is being debugged. It consists first of an acoustically quiet loading apparatus which permits indentation loading of a plate together with XY translation and an encompassing Faraday cage for rf screening. A set of six wideband sensitive transducers is mounted on the plate surrounding the indenter in an array. These signals are then preamplified, bandpass filtered at 0.01 to 2.5 MHz, and given final amplification up to 100 dB gain in a custom-designed multichannel set of main amplifiers. The data are captured by a set of six 8-bit 2048 point digital recorders. A custom built high-speed interface and associated data bus can dump all of these channels and rearm for the next transient of AE with a turn-around time on the order of 10 ms. Thus the multichannel system is essentially complete and following debugging will be ready for the critical set of experiments to validate the multichannel approach.

(3) Experimental AE source simulation. An Nd-Yag laser is being used as a highly reproducible thermoelastic AE source for simulating defects such as microcrack dipoles in a systematic set of studies which is in the completion stages. The reproducibility of the source permits the use of a single channel for mapping the stress wave fields generated by the thermoelastic source. These experimental results await validation by the theoretical curves generated for these configurations in a stainless steel plate using the plate codes generated previously in these studies.

(4) Rapid solidification studies. AE has great potential for the study of dynamic materials events such as rapid solidification, where stress waves may be generated by thermoelastic contractions, by phase change contractions, by defects such as cracks produced during solidification, or by other solidification phenomena. Virtually no information of this type has been obtained for obtained rapid solidification and results of this type are expected to be of great interest in this field.

Two approaches are being made; the first is a wideband technique for use with a laser, where solidification can be kept rapid enough to capture the virgin stress waves before reflected waves distort the signal. This technique would be useful for solidification events less than about 100 us in length. So far this approach has been limited to detection of vaporization phenomena. The second technique is a low frequency narrow bandwidth method which is suited for solidification phenomena of duration of the order of a ms or more, such as is obtainable with a steady-state melt generated by an electron beam. For these conditions, exploratory measurements have been made which show transducer ringing, a sign of acoustic rather than electrical (noise) phenomena. Conditions are being established to optimize the signal-to-noise ratio and verify the phenomena. Verification in part can be accomplished by comparing signals generated in the solid state by thermoelasticity and signals generated during solidification from a steady-state melt following the termination of the beam current.

Magnetic Measurements
Subtask 6 of Task 12142

L. J. Swartzendruber

Magnetic methods of nondestructive evaluation utilize the relationship between material properties and static or slowly varying magnetic fields. They find wide application both on the production line and in the field and, where usable, provide a sensitive, rapid, and often relatively inexpensive test method. Uses include measurement of important metallurgical properties, detection of harmful defects, and measurement of coating thickness.

One of the most extensively used techniques in magnetic NDE is the magnetic particle method. The application of this method is currently guided by empirical rules for the amount of magnetization required to achieve the desired results. Also, there is no acceptable method for independently testing magnetic inks. The first steps in placing magnetic particle inspection on a more quantitative and reproducible basis are an understanding of how the leakage field from a defect is influenced by the defect geometry and level of magnetization reached by the material, and a detailed description of the influence of the leakage field on the formation of an indication by the magnetic ink.

Previous investigations of magnetic particle defects have led us to propose a detectability criterion for defects under magnetic particle inspection. Using this criterion, and a phenomenological description of the magnetic leakage field from cylindrical defects, the detectability of cylindrical defects as a function of defect depth, defect size, and applied magnetic field can be predicted. In order to apply this criterion, and to test its validity for more complicated geometries, it is necessary to calculate leakage fields from more complicated geometries. Computer modeling techniques to perform this function are being developed.

Results have been obtained from a finite difference model using a square grid and defects with a square cross section placed at various depths below the sample surface. In the initial form of this model a linear isotropic magnetic medium was assumed. After the model results were obtained they were least squares fitted to the field expected from a magnetic dipole. (The field from a cylindrical defect in a linear isotropic medium can be calculated analytically and is a dipole field.) Figures 11 and 12 show the fields perpendicular and parallel to the surface of the material, respectively. It can be seen in these figures that the field from a square defect is almost indistinguishable from a dipole field. Note that the field parallel to the surface has a large bias field of 30 gauss. This added field is just the applied field which was parallel to the surface. Using these results a quantitative comparison can be made with the field from a cylindrical defect. The square defect gives a leakage field approximately ten percent higher than that from an inscribed cylinder.

It is planned to continue these calculations for different geometries such as rectangles and slots. In addition, the program is being modified to cover the more realistic case on nonlinear media. For this case, a finite element method will be employed in an attempt to reduce the expected large increase in computer time. The outcome of these calculations, along with further experimental

measurements, will be used to develop a critically needed specification for the applied field necessary to detect defects of a given size and geometry. The results will also be useful for the leakage field measurement method which is a technique of growing use in the field of nondestructive evaluation.

Magnetic Particle Inspection Standards
Subtask 7 of Task 12142

L. J. Swartzendruber

This project was initiated by the Specification and Technical Data Branch of the Army Materials and Mechanics Research Center, Watertown, Massachusetts. Military Specification MIL-M-11472, Magnetic-Particle Inspection; Process for Ferromagnetic Materials, is being reviewed for proposed revision or cancellation and replacement by Military Specification MIL-STD-271, Military Specification MIL-I-6868, or American Society for Testing and Materials Recommended Practice E709-80. The contents of these documents are being compared with current state-of-the-art practice in magnetic particle inspection as revealed by industrial practice and available literature. A review of current applicable Military Standards, Aerospace Materials Specifications, and American Society for Testing and Materials documents suggests that the Military Specifications are in need of extensive revision. Accordingly, a draft version of a revised MIL-M-11472 is being prepared. An attempt is being made to make the revised specification as complete and self-contained as possible. Feedback from Department of Defense users then will be used to eliminate or revise portions as deemed necessary.

Scanning Electron Microscope
Subtask 8 of Task 12142

David B. Ballard

The NML-SEM facility of 2 SEM's and associated equipment has continued to provide microstructure studies for a wide range of research activities at NBS. An estimate of over 1,000 hours includes both individual operation and support services. Some examples of support services provided are as follows.

(1) Several samples of different materials, such as 2024 aluminum and welds in pressure vessel steel, that had been subjected to surface modification by rapid melting by laser and electron beams, were examined. These samples also had been monitored by acoustic emission techniques during processing. Details of surface crack micro topography observed by the SEM correlated well with the recorded acoustic wave forms.

(2) Samples collected at four levels within the solidification chamber during atomization of a Pb-Sn alloy were examined for particle size and shape (figure 13). A large variation of size ranges was found at all levels; however, the sample nearest the injector nozzle had significantly smaller particles, some under 0.1 μm in diameter.

(3) The sample surface of four different compositions composed of Al-Ag was melted with a pulsed laser. Metallographic cross-sections of these samples were observed in the SEM. Numerous photomicrographs of the heat effected zone and altered fine microstructure were made for further study.

High carbon, high tensile strength rods in the as-drawn then stress relief tempered condition are used as tension members in prestressed concrete. Specimens of fractured rods tested under three different laboratory conditions were submitted by the Chemical Stability and Corrosion Division for fractographic analysis. Also, SEM photo micrographs of metallographic cross section and longitudinal sections were included to determine the fine pearlite grain size and preferred orientation. Results of this analysis will be published as an NBSIR entitled, "A Fractographic and Metallographic Study of External Induced Fracture of Steel Tendons Used in Prestressed Concrete," by D. B. Ballard, C. H. Brady, C. E. Johnson and E. N. Pugh. A request was received from Bendix Electrical Components Division that involved the application of a calibrated SEM technique to measure nominal one micron thickness of gold electroplated onto beryllium-copper rods. This technique was described in a prior publication by F. Ogburn and D. B. Ballard. The problems experienced by Bendix included wide disagreement (25 to 30 percent) between their optical and SEM thickness measurements made on samples to be used as manufacturing control standards. Preliminary examination of two thickness samples as polished by Bendix indicated a need for improved metallographic surface preparation. After the samples were properly prepared the observed quality of the two electroplatings were different, one was much smoother than the other. This observation could have accounted for some measurement difficulty in the optical measurement effort. During the comparison of the NBS optical vs SEM measurements, using a properly etched sample of SRM-484 for control, it was found the magnification of the metallograph used was measured to be 1,043X instead of 1,000X as indicated by use of an optical stage micrometer. After applying a correction to the optical and SEM magnifications, measurement of the gold thickness on the two samples, agreement between the two techniques was within the range of 10 percent. The technique of measuring the SEM wave form midpoints (Full Width Half Maximum) was suggested as a reproducible procedure if the samples were prepared in an identical way and photomicrographs made under known magnification control by a careful operator.

The outside purchase of the SEM-SRM 484 magnification standard has continued at an average rate of six units per month for the period of October 1980 through August 1981. This SRM is the control sample that is referenced in Part II, E766-80, of the 1981 ASTM Standards available September 1981. A schematic diagram illustrating the construction of the magnification standard and a SEM photomicrograph of the 1 to 2 μm space taken at a nominal magnification of 20,000X are shown in figures 14a and 14b. As a complement to the above ASTM standard, the first draft of "Standard Practice for SEM Performance Characterization," has been submitted for review by E04.1107 ASTM Subcommittee. Work has begun on the development of a new SEM sample whose criteria are especially suited for this test performance.

Eddy Current Standards
Subtask 9 of Task 12142

A. J. McAlister

The eddy current method is widely used in both the ferrous and nonferrous metals industries for nondestructive detection of flaws such as cracks, inclusions, and variations in composition and microstructure in metals and metal parts via local changes in electrical conductivity. Primary conductivity

standards are needed for reliable execution of this work, but to date, this need has been supplied by industry itself. The necessary range of conductivity for industrial testing is from 5.85 to 58.5 MSm^{-1} (1 to 100 percent IACS). NBS is currently acting to provide Al alloy standards in the mid-range of 17 to 35 MSm^{-1} (29 to 60 percent IACS). One hundred sets of four aluminum samples covering this conductivity range have been supplied to the Electrical Measurement and Standards Division for final calibration.

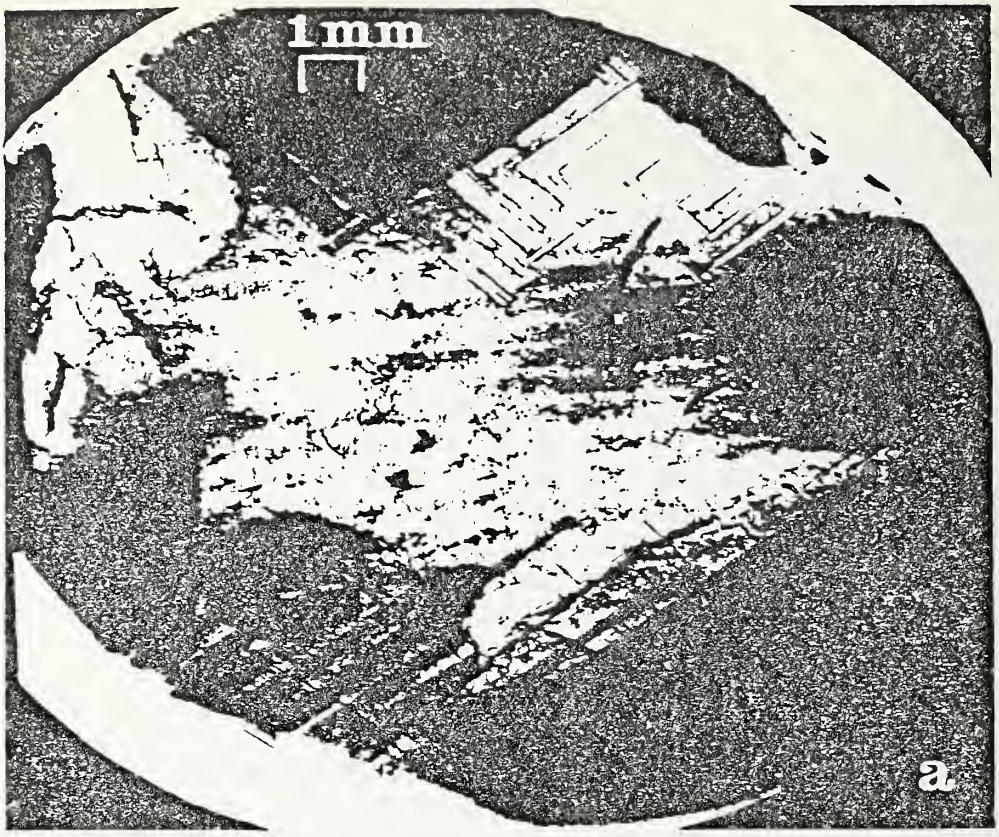
The properties desired in a primary conductivity standard are long term stability, durability, and low magnetic susceptibility. (In testing of high susceptibility steels, normal practice has been to apply a saturating magnetic field to reduce the differential permeability to a value near that of vacuum.) Hence, elemental metals and alloys of equilibrium phase composition, upon which stable nonconducting surface layers can be formed, are desirable. The surface properties are important not only for durability, but for reproducible lift-off behavior as well.

The overall aim is the selection of metals and alloys suitable for primary conductivity reference standards in the 5.85 to 14.6 and 35 to 58.5 MSm^{-1} conductivity ranges, and the preparation of specifications for their preparation and fabrication. Nine candidate materials which appear suitable on the basis of their reported physical properties and probable homogeneity and phase and surface stabilities have been identified.

The following metals and alloys will display conductivities within] percent IACS of the stated values:

Material (w/o)	Conductivity (% IACS)
OFHC Cu	101.0
1.3 Zn + Cu	85.0
2.4 Zn + Cu	72.0
2].5 Zn, 2.5 Al + Cu	23.0
7 Al + Cu	17.0
1.5 Si + Cu	12.0
3.0 Si + Cu	7.0
Commercially pure Ti	3.5
8 Al, 1 Mo, 1 V + Ti	1.0

For these materials we are investigating the likelihood of attaining the desired metallurgical and surface properties. Questions concerning these materials and their preparation--quality of starting materials, conditions of melting and solidification, heat and mechanical treatment, possible adverse affects in cutting, machining, and surface preparation--are being addressed by a search of the literature and an inquiry of industrial practitioners about their experience and methods and by specific research as necessary.



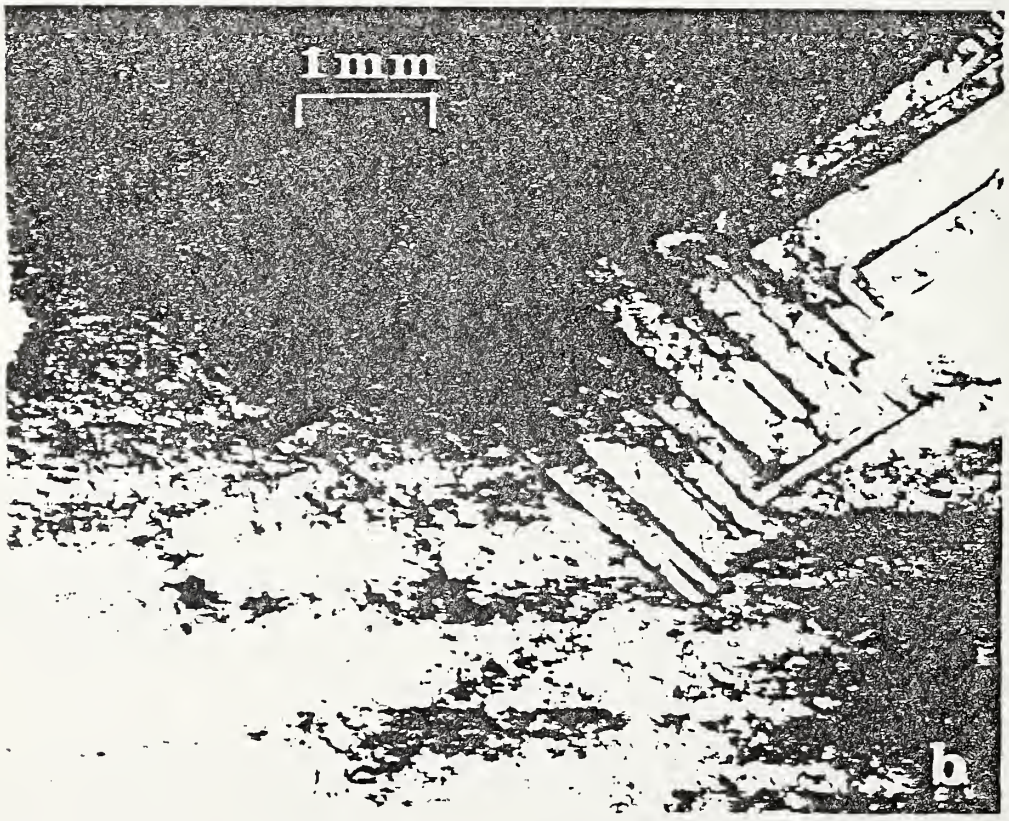


Fig. 1 Transmission X-ray topograph of a thick (μL=10) Ni crystal obtained with a nuclear emulsion without x-ray magnifier. (a) Full-view x-ray topograph. (b) Enlargement of the top-center region of (a).

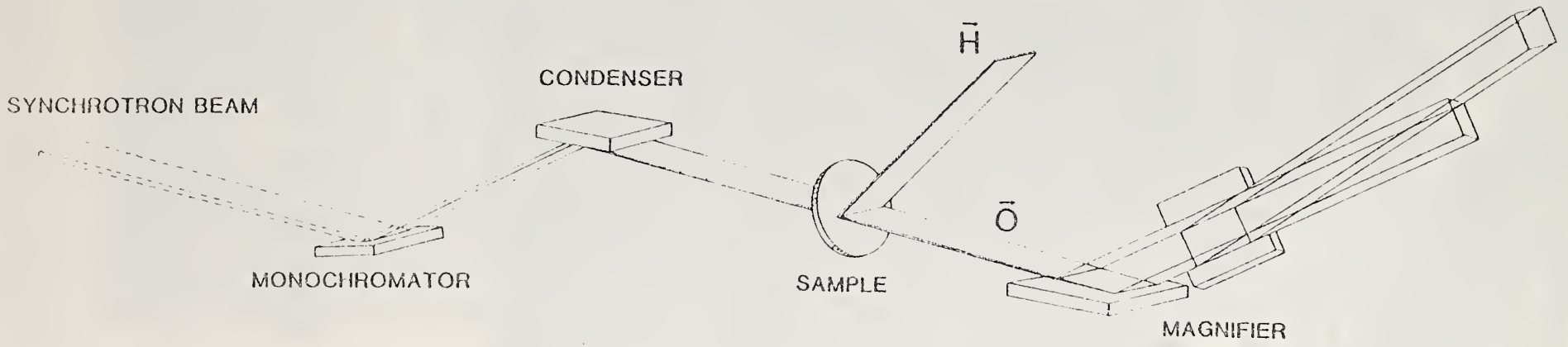


Fig. 2 Arrangement of flat crystal diffraction elements used to produce magnified images of x-ray topographs and microradiographs.

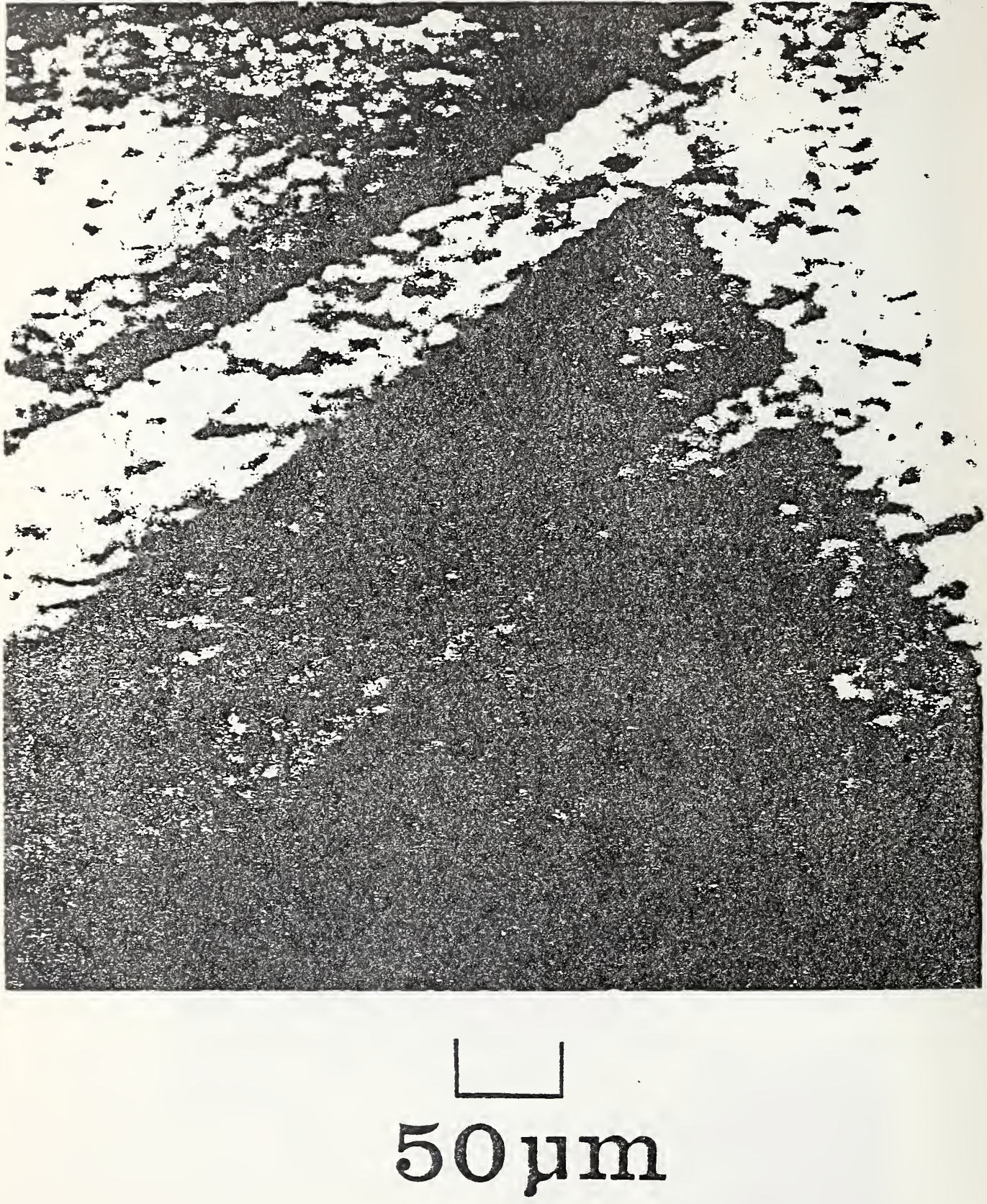


Fig. 3 X-ray transmission topograph showing the magnetic domain structure of a Ni crystal observed with the 20x x-ray magnifier and recorded on instant film.

Fig. 4 Magnetic domain wall motion contained in a sequence of enlargements from frames of a movie film negative which was made from video tape images using a high-resolution monitor. The motion is due to the application of a magnetic field.

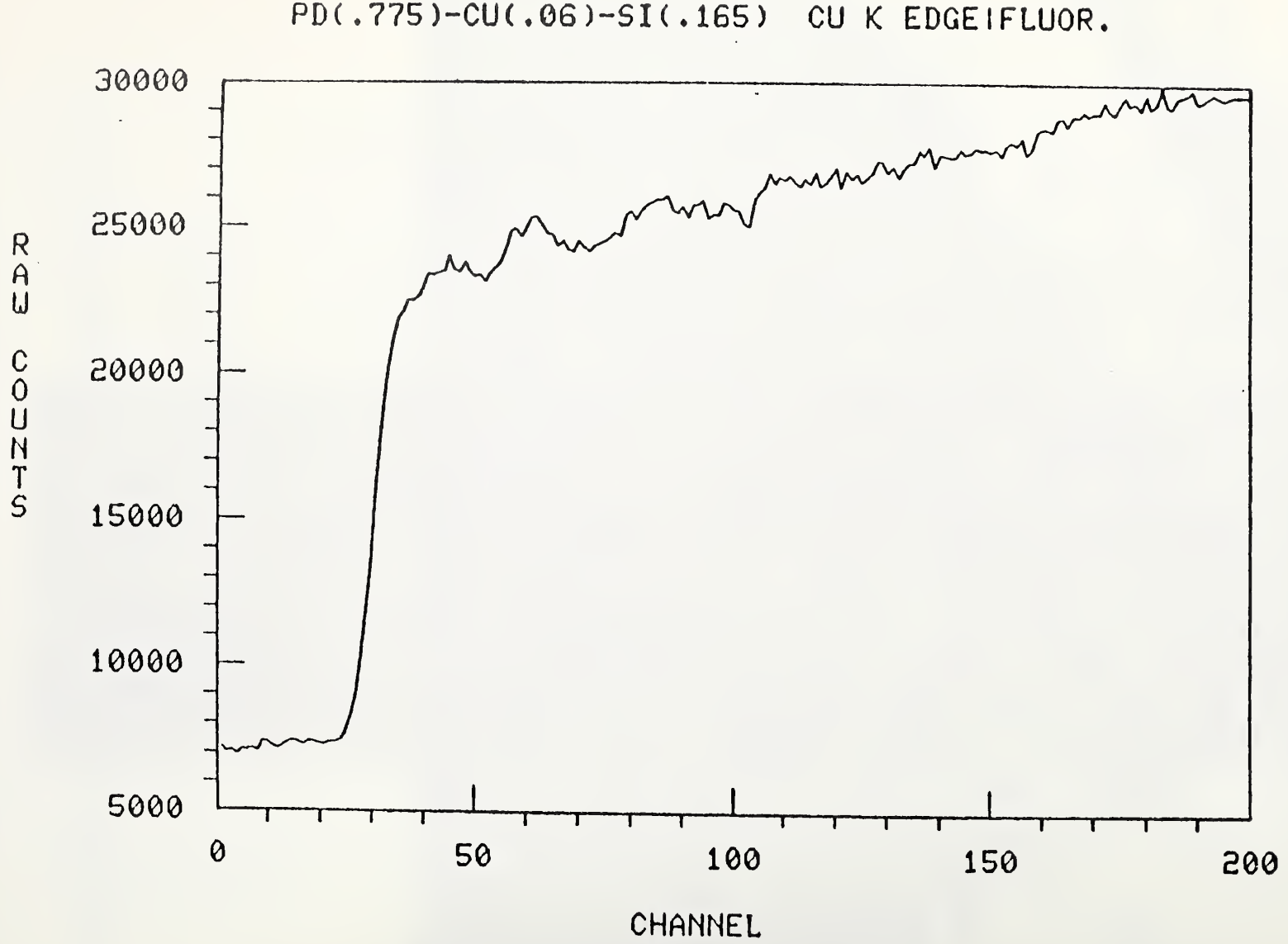


Fig. 5 Cu-fluorescence EXAFS from $Pd_{.775}$ $Cu_{.06}$ $Si_{.165}$

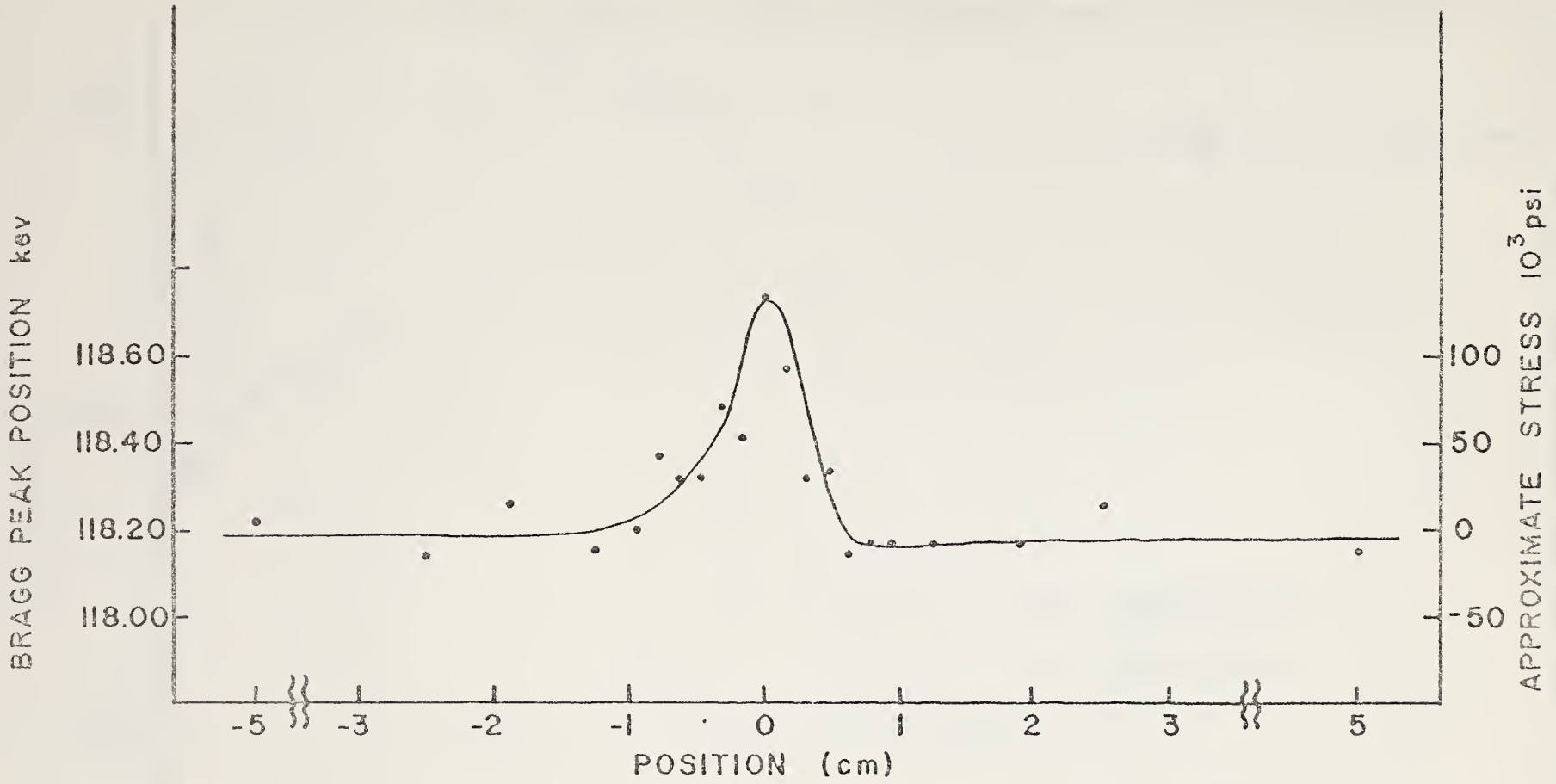


Fig. 6. Residual stress distribution across a welded zone in an Alaskan pipe line steel 14.6 mm thick. This mapping is obtained at a scattering angle 5° in the transmission geometry using (211) diffraction. Positive values of stress represent compression.

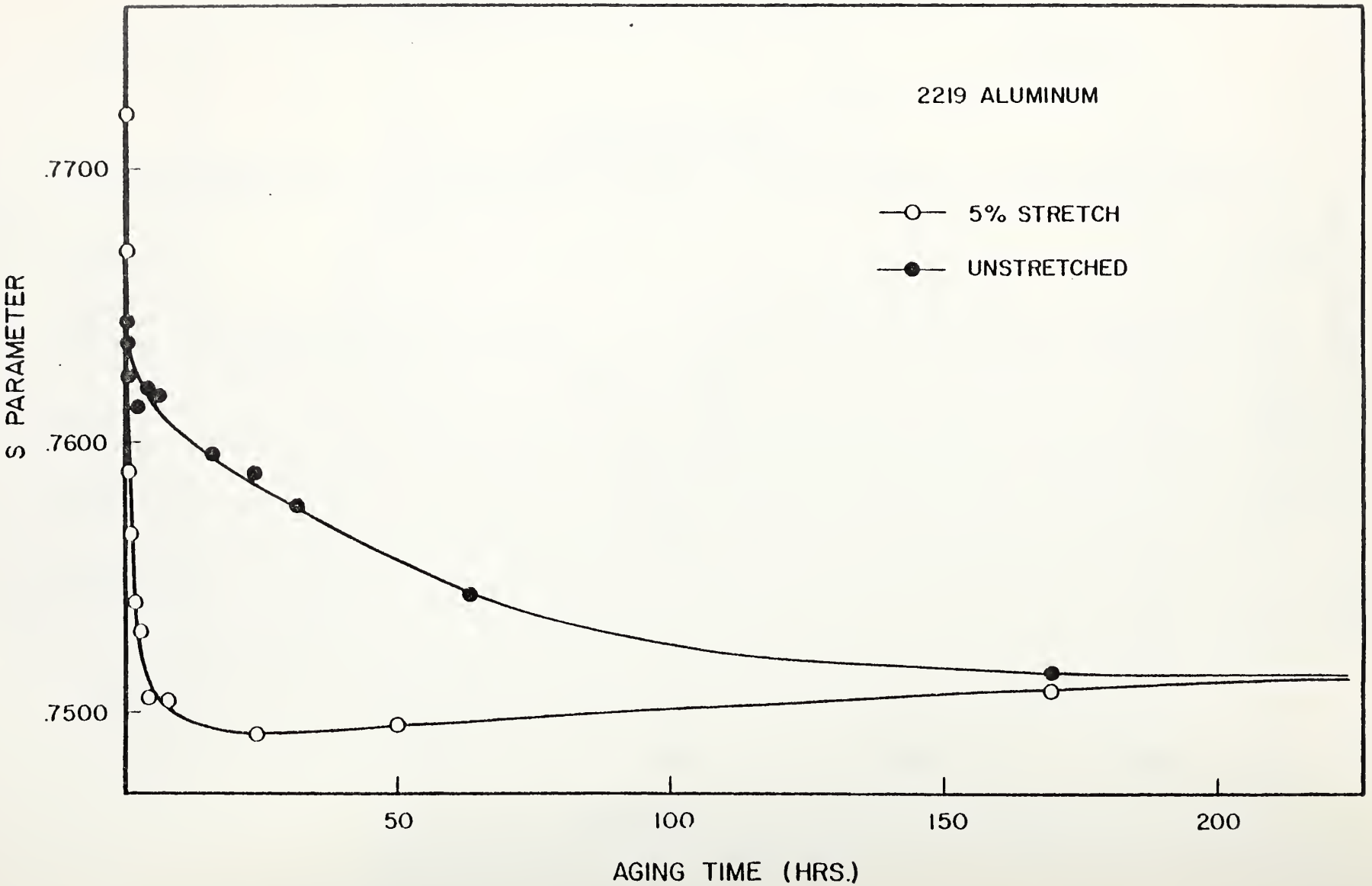


Fig. 7 Positron S-parameter for 2219 Alloy aged at 172 °C. Stretch was applied prior to aging treatments.

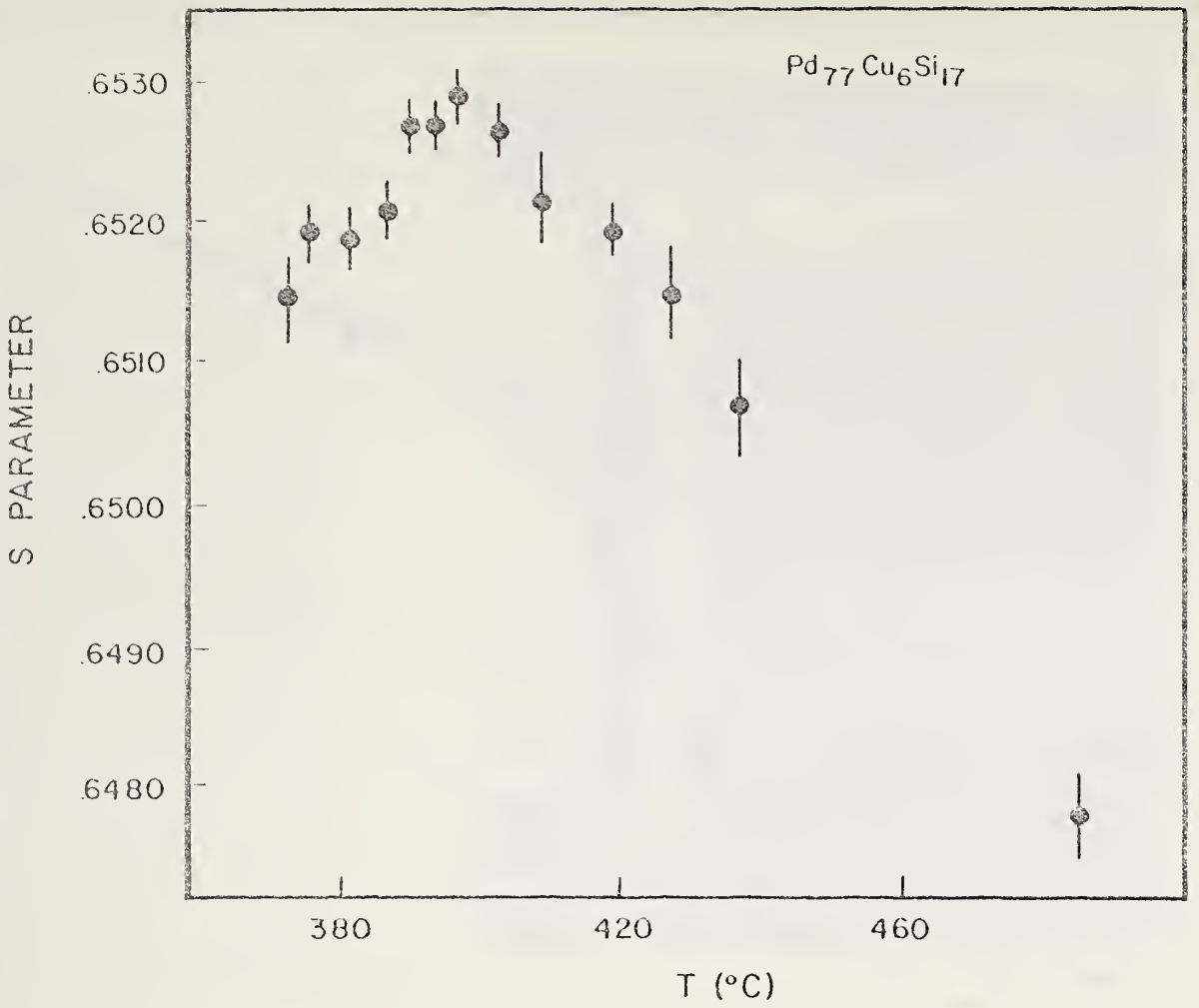


Fig. 8 Positron S-parameter for Pd_{77} Cu_6 Si_{17} alloy heat treated at various temperatures. Crystallization begins at about 380 °C.

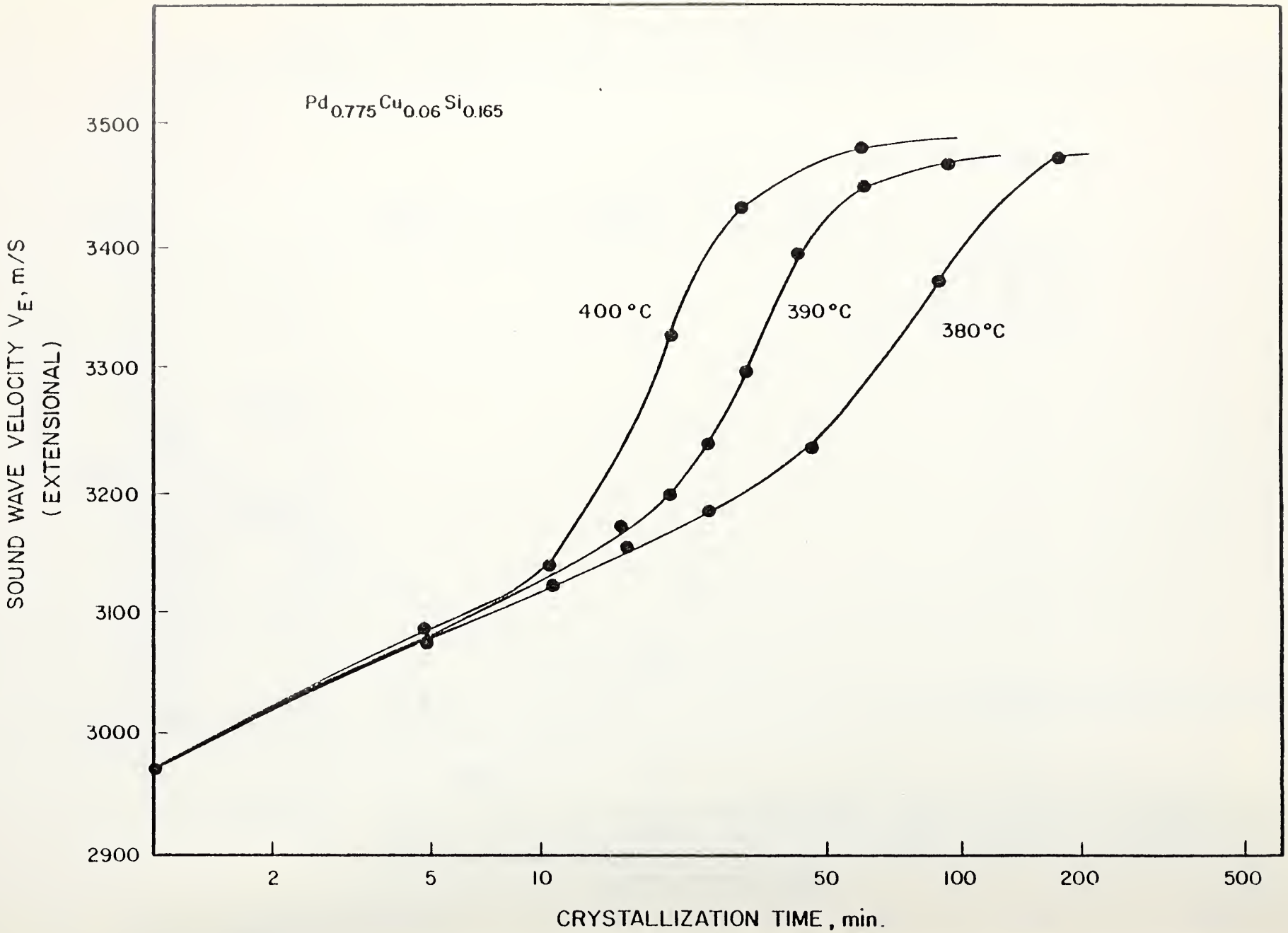


Fig. 9 Variation of the sound wave velocity as a function of crystallization time during the amorphous to crystalline transition in Pd-Cu-Si at 380, 390, and 400 °C.

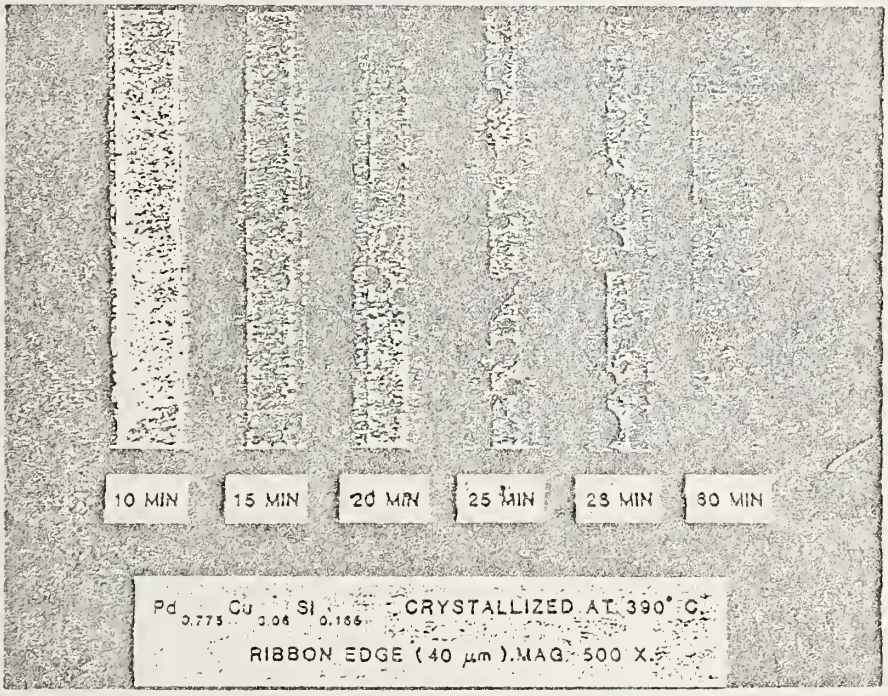


Fig. 10 Changes in microstructure as a function of time during the amorphous-to-crystalline transition in Pd-Cu-Si at 390°C. View from the ribbon edge.

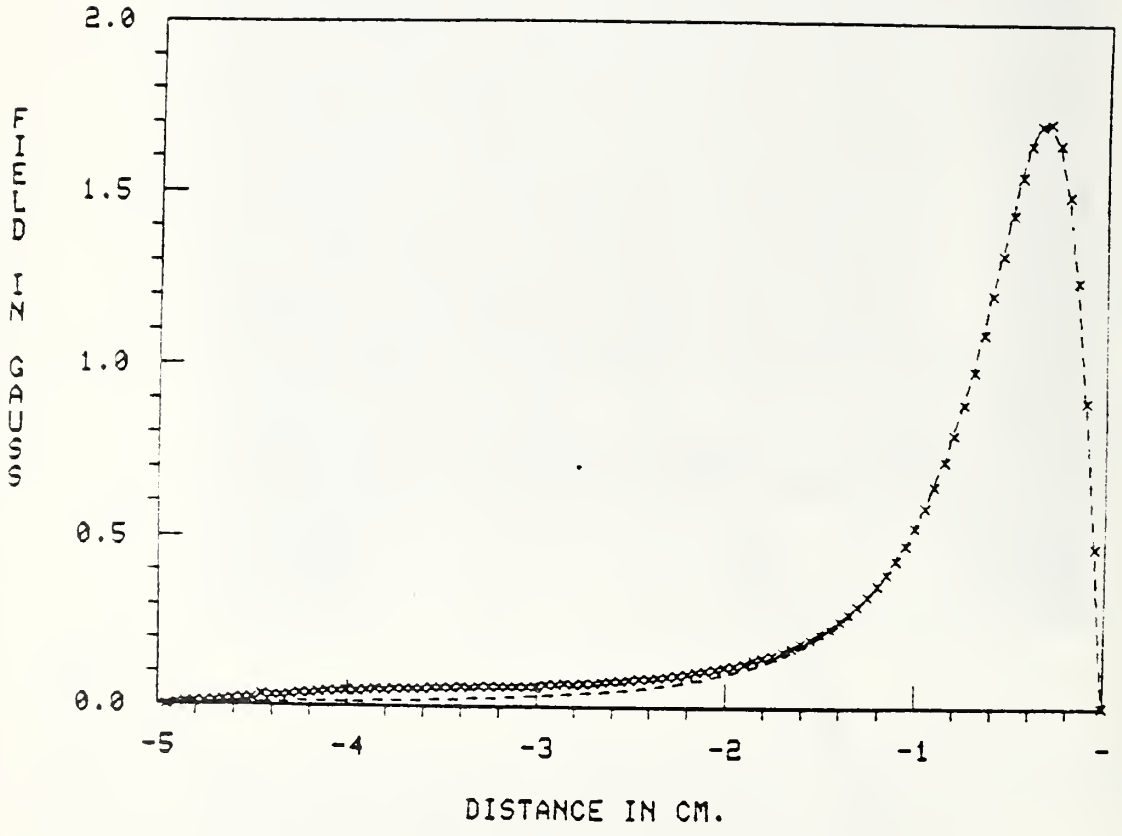


Fig. 11 Magnetic leakage field perpendicular to the sample surface versus distance from the defect center (the field is antisymmetric about the origin; only the left half is shown). The applied field is 30 gauss parallel to the sample surface and the leakage field is assumed to be measured 0.3 cm above the surface. The defect cross section is a square 0.2 cm below the surface. The crosses are the calculated field and the dashed line is a least squares fit to a dipole field.

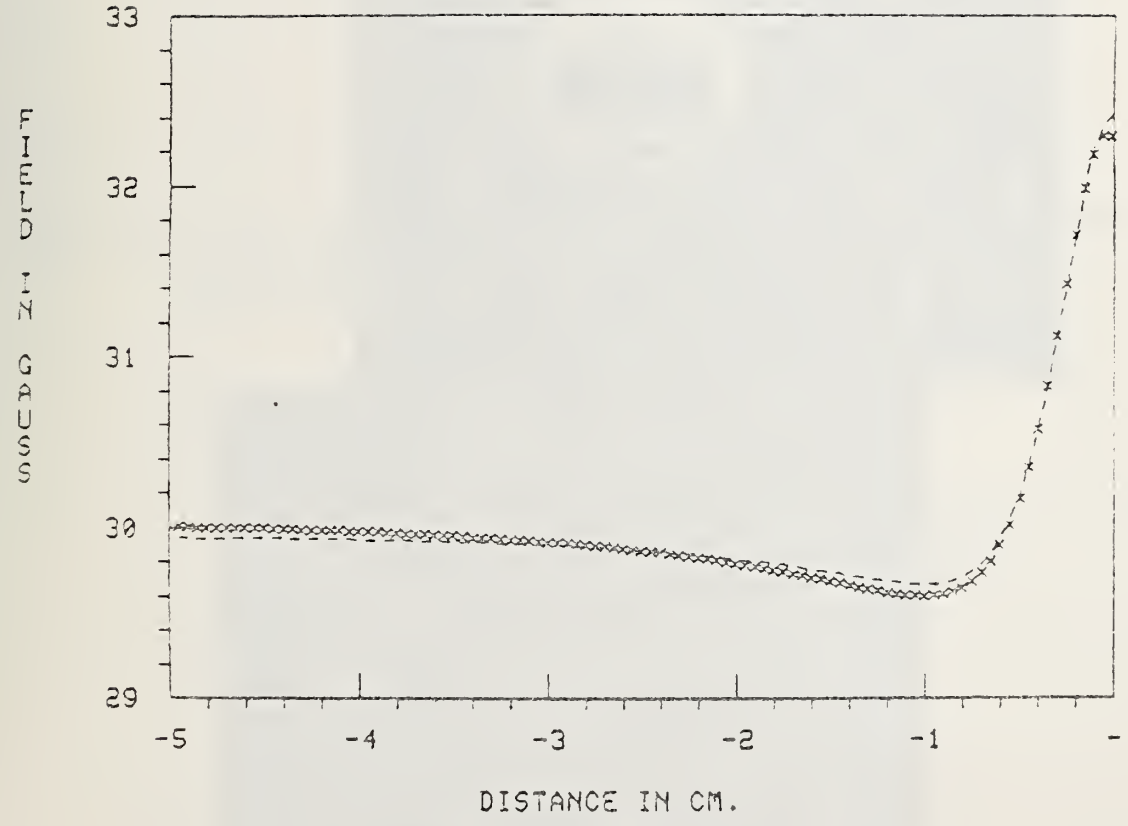


Fig. 12 Magnetic leakage field parallel to the sample surface versus distance from the defect center (the field is symmetric about the origin; only the left half is shown). The applied field is 30 gauss parallel to the sample surface and the leakage field is assumed to be measured 0.3 cm above the surface. The defect cross section is a square 0.2 cm on a side with the top 0.2 cm below the surface. The crosses are the calculated field and the dashed line is a least squares fit to a dipole field.

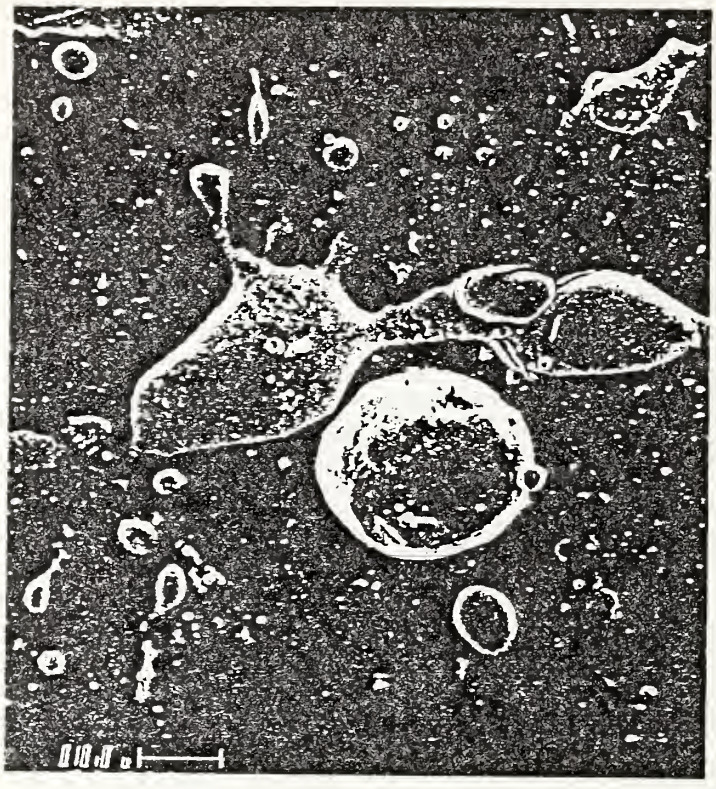


Fig. 13. SEM photomicrograph of atomized Pd-Sn alloy collected at the second level within the solidification chamber. 1,000X.

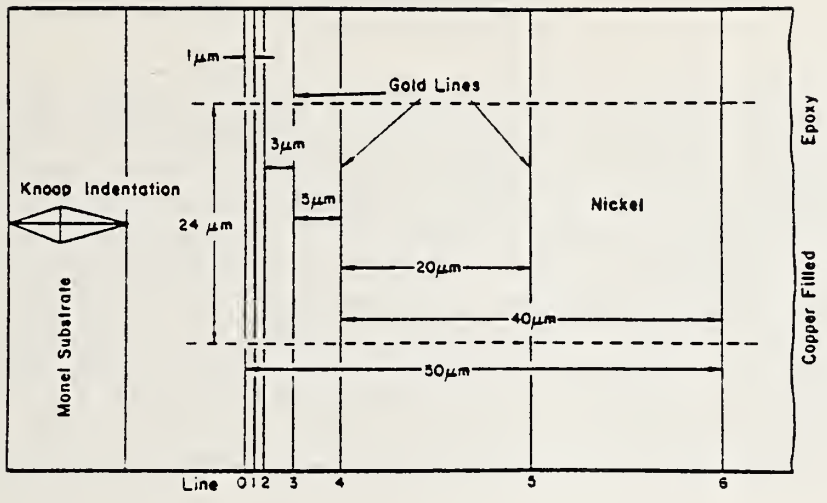


Fig. 14a. This schematic diagram shows the calibrated area and the nominal distances between each of the gold lines in NBS-SRM484.

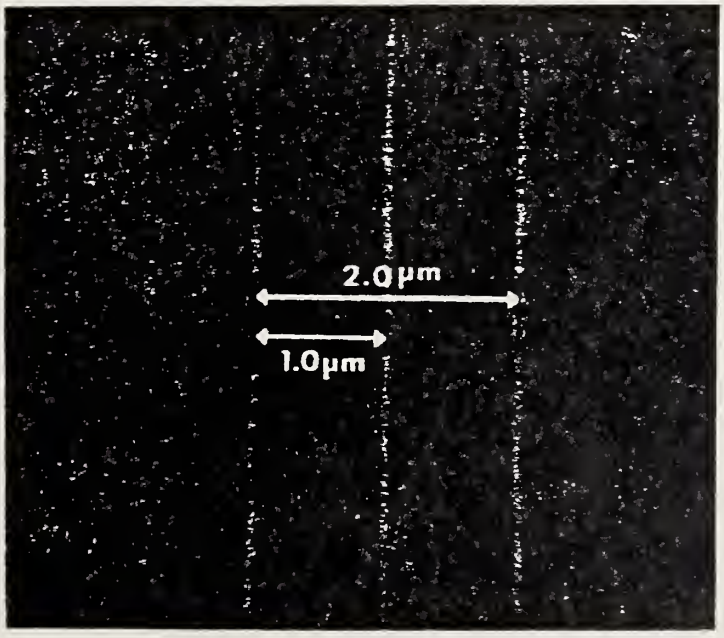


Fig. 14b. SEM photomicrograph of lines #0, 1 and 2 at a nominal magnification of 20,000X.

METALLURGICAL PROCESSING FOR ALLOY DURABILITY
Task 12143

Metals processing research plays a central role in the Division's activities. The properties of alloys depend on their compositions and microstructures, which are dictated by their processing history. Thus, the effective performance of components in societal use depends strongly on solidification and solid state transformation processes, diffusion, and other kinetic changes that alloys undergo during production and shape forming operations. The central objective of this task is to develop data, measurement techniques, theory, and predictive models relating variables during metallurgical processing to microstructures, hence properties and performance of alloys. In addition, the Diffusion in Metals Data Center of the National Bureau of Standards is located in this group. This Center is a national metallurgical resource that provides a central source of extensive evaluated data on diffusion to the technical community at large.

New activities in this task are being directed toward innovative metals processing technologies, particularly rapid solidification. Processing techniques which produce rapidly solidified surface layers, powder, and ribbon are being used to determine the relation of processing conditions to the microstructure and composition distributions in rapidly solidified alloys. An electron beam surface melting facility has been developed to provide quantitative measurement and control of energy input during surface modification. As new equipment, a vacuum melt spinning device to produce metallic glass has been constructed, and an electrohydrodynamic system to form very fine, rapidly solidified alloy powder is being put into operation. One goal of these rapid solidification studies is to establish relations between solidification velocities and properties of the resulting alloys. In Pd-Cu-Si, it was found that the transition from crystalline to amorphous alloy as solidification rates were increased can be related to the diffusional sorting necessary to allow separation of constituents into two-phase lamellar structures and to the effect of alloy composition on formation of dendritic crystals. In electron beam studies on Al-Ag, the high velocity solidification regime where, according to a predictive model developed here, planar solidification, avoiding dendritic segregation, may be obtained is being investigated.

New experimental techniques and predictive models also are being developed in other areas of metallurgical processing. For example, ultrasonic techniques are being developed to provide real-time in situ measurements of solidification interfaces and velocities, which could allow feedback and control during conventional solidification or continuous casting. NBS work is focussed on the measurement factors inherent in possible use of these methods for process control. In particular, spacial averaging techniques have been applied to improve substantially the signal-to-noise ratios in test specimens where scattering from grain boundaries was a problem. Such grain scattering problems have been limiting factors in ultrasonic attempts to determine skin thickness in steel continuous casting.

Convection in solidifying alloys can strongly influence the compositon distributions and defect structures. In order to analyze the convection arising from surface tension gradients (Marangoni effect) and from simultaneous temperature and composition gradients (solutal convection), surface tension and solutal convection measurements are being made. A major feature of the surface tension work is the design of novel measurement techniques which allow Auger measurements of impurity and surface alloy concentrations to be made on the liquid surface simultaneously with surface tension measurements. Solutal convection is being measured in a transparent material which models the solidification behavior of metal alloys but allows direct observation of convection velocities.

Alloying processes produced by diffusion-induced grain boundary migration are being measured. This phenomenon shows promise of providing a new method for surface modification, allowing production of diffusion alloy coatings at unusually low temperatures. In recent work, grain boundary migration has been found in Au-Zn and Cu-As alloys, as well as further examples in Cu-Zn. In each of these alloys, it appears that the volatile constituent, Zn or As, which is produced as a vapor from an alloy source, diffuses into the matrix metal, Cu or Au, along grain boundaries. Because of the low temperatures (200 °C to 400 °C) diffusion does not occur directly into the interiors of the grain volumes. Instead, migration of the grain boundaries is induced because of the diffusional flow of Zn or As into the boundaries; and the volume through which the boundaries pass becomes alloyed. This process yields remarkably large effective volume diffusion coefficients at temperatures where normal volume diffusion is negligible.

In diffusion data work a comprehensive evaluation has been made of mass transport data in copper alloys. A 300-page review which supplements previous work done here on these alloys has been completed. The copper alloys are being used as a test system for the work of computerizing bibliographic and other information for the Diffusion in Metals Data Center.

Computerization of temperature data acquisition and analysis has aided research on macrosegregation in 2219 and 2024 aluminum alloys produced under various cooling rates. In addition, a complete series of instrumented heat treatments has been conducted on these alloys to determine the effects on microstructures and properties resulting from interrupted or slack quenching from solution heat treatment temperature.

Task members were active in organizing a national conference on Rapid Solidification Technology, co-sponsored by COMAT and hosted by NBS in Gaithersburg, Maryland, July 1-2, 1981. This conference was directed toward planning Government-wide strategy for exploiting this new technology. Task members serve on advisory committees for the Solar Energy Research Institute and the National Aeronautics and Space Administration; on boards of international journals on diffusion and crystal growth; and on working committees of the ASTM, AIME, American Society for Metals, and the National Materials Advisory Board.

Rapid Solidification
Subtask 1 of Task 12143

W. J. Boettinger, S. R. Coriell, R. J. Schaefer, J. W. Cahn

This project is focused on increasing knowledge of the kinetic processes which occur during the rapid solidification of alloys. A broad class of experimental results on rapidly solidified materials are difficult to understand because existing theory needs extension to higher solidification velocities and because accurate quantitative experiments are difficult to perform due to the high cooling rates and small specimen sizes. The current work of this project is directed toward two areas: (1) microsegregation as determined by the shape of the freezing interface, and (2) glass formation by rapid cooling of eutectic alloys. In these areas, new theoretical predictions are being examined experimentally but also experiments are being performed to direct theoretical efforts. Summaries of progress in these areas are reported below.

(1) Microsegregation and Stability at the Solidification Interface. One of the long-term goals of this research is to predict, theoretically, the amount of microsegregation in rapidly solidified alloys as a function of the processing conditions. For constant velocity solidification, morphological stability theory has been used to determine the conditions under which a planar solid-liquid interface is stable to small perturbations and hence when microsegregation does not occur. The theory predicts planar solidification at low and high velocity with a regime of instability at intermediate velocity. The high velocity prediction (absolute stability) may be related to the elimination of microsegregation observed in some rapidly solidified alloys. Evaluation of the morphological stability predictions for a given alloy requires knowledge of a number of thermophysical properties, e.g., liquid diffusion coefficients and solid-liquid surface free energy. If local equilibrium prevails at the solid-liquid interface, reasonable estimates of these properties can be made and the conditions for production of homogeneous alloys estimated. With increasing solidification velocity, increasing deviations from local equilibrium at the solid-liquid interface are expected. While morphological stability theory has been extended to account for deviations from local equilibrium, the resulting expressions contain a number of quantities, e.g., the dependence of solute distribution coefficient on solidification velocity, which have not been measured. Future experiments are planned to determine this dependence.

When rapid solidification occurs at velocities less than that required for absolute stability, it is to be expected that alloys will exhibit microsegregation. Another effort of this research is to develop a quantitative theory of microsegregation, i.e., alloy composition as a function of position on a microscopic scale. The formulation of the relevant differential equations for the temperature and solute fields and the boundary conditions at the solid-liquid interface is straightforward. However, the numerical solution of the resultant free boundary problem and calculation of solute segregation is not feasible at present despite considerable progress that is being made by a number of research groups using finite element techniques. Our present effort has involved a number of simplifying assumptions in order to obtain more tractable problems. For example, in collaboration with R. F. Boisvert, R. G. Rehm, and R. F. Sekerka the lateral solute segregation (macrosegregation) that results from a curved solid-liquid interface during steady state directional solidifi-

cation of a dilute binary alloy has been calculated. For a given interface shape, the solute segregation depends on the distribution coefficient k and on the dimensionless parameter (VL/D), where V is the solidification velocity, L the cell size, and D the solute diffusion coefficient in the liquid. The details of the calculation are given in an article published in the Journal of Crystal Growth. For both very large and very small values of (VL/D) the segregation is small while for intermediate values of (VL/D), dependent on k, the segregation is maximum. The theory permits calculation of solute segregation from an observed interface shape. However, cell size and interface shape are actually functions of interface velocity and the functional relationships require solution of the general cellular growth problem.

An experimental program to investigate the prediction of absolute stability is now being conducted with aluminum-silver alloys. In these alloys solidification velocities of the order of 1 to 10 cm/s should be required. Rapid solidification is produced by electron beam surface melting of the alloys, and the interface velocities and gradients are numerically computed. Several different modes of melting, such as pulsed stationary spots or spots moving at constant velocity, can be used. Calorimetric measurement of the energy absorbed by a flat aluminum surface was used to account for the influence of electrons which are backscattered after losing a fraction of their energy. In addition, methods were developed for mapping out the distribution of energy within the electron beam, which is highly non-gaussian under some focus conditions. It has been found possible to produce beams with energy profiles which correspond well to the conditions assumed in computer models of surface melting.

In experiments in which the beam was moved at constant velocity across the surface of Al-Ag alloys, cellular structures were seen even under conditions where plane front solidification was expected to be stable. Although this observation may indicate that the limits of the region of absolute stability have not been correctly predicted, it is important to also consider that during the melting and freezing cycle these samples passed through conditions where instability was expected before attaining the conditions of predicted absolute stability. Thus the surface melting experiments must be interpreted by considering the entire sequence of interface velocities and gradients which occur during the melt cycle, and also the rate of growth of perturbations when they are unstable and the behavior of cellular interfaces which enter regions where plane fronts are stable. Current efforts are directed toward identifying the melt cycle conditions which will completely bypass the region of morphological instability. In addition, we plan to evaluate the behavior of solidification transients to estimate their influence on the applicability of steady state morphological stability theory.

(2) Metallic Glass Formation. Research continued on the relationship between eutectic solidification and the formation of metallic glass. The theory of how rapidly one needs to solidify to obtain a glassy structure has usually focused on the nucleation of the solid phase as the difficult step in crystallization. In the present work, the focus instead has been on the growth process. Due to thermodynamic considerations, a large range of compositions about many eutectics, especially those involving line compounds, must crystallize from the liquid as multiphase solids even if that crystallization is far from equilibrium. This range lies between the T_o curves for the phases in the eutectic. In this composition range (partitionless) crystallization is forbidden, and the maximum crystallization rate will depend on the

details of the diffusive sorting of the components in the liquid into the crystalline phases and the creation of crystal-crystal interfaces. In particular the maximum eutectic growth rate seems closely related to the minimum cooling rate requirements to form metallic glass for compositions near eutectics. The present work investigates the behavior away from the eutectic.

Experiments on a model glass forming alloy (Pd-Cu-Si) have been conducted using rapid directional quenching. Thin alloy-filled quartz tubes (0.75 mm i.d. x 1.5 mm o.d. x 10 cm long) are quenched in the axial direction from a furnace into liquid Ga at controlled speeds. When the microstructures are aligned in the axial direction the growth velocity is equal to the quenching velocity. This feature permits the characterization of the critical growth conditions required to form metallic glass as well as the microstructures obtain at sub-critical growth conditions. Figure 1a shows the observed microstructure as a function of growth rate for the compositions shown in figure 1b. The results show that for low copper contents the transition from dendritic growth to eutectic growth with increasing growth rate determines the critical conditions for the avoidance of crystallization and the formation of metallic glass. For high copper contents, the formation of dendritic crystals directly from the melt (even when the eutectic is growing nearby) prevents the formation of completely glass structures. Still, the interdendritic regions are amorphous. The formation of these crystallites is related to the proximity of the high copper alloys to the T_o surface for the κ phase (see figure 1b). A paper on this subject "The Effect of Alloy Constitution and Crystallization Kinetics" by W. J. Boettinger will be published in the Proceedings of the Fourth International Conference on Rapidly Quenched Metals.

Ultrasonic Measurement of Solid/Liquid Interface Position during Solidification and Melting of Metals
Subtask 2 of Task 12143

R. L. Parker

Ultrasonic techniques are being developed to provide real-time, in situ, nondestructive measurement of the position, velocity, and shape of solidification interfaces in opaque materials. The use of pulse-echo ultrasonic flaw detectors to detect the presence and location of cracks, voids, and other flaws in metals and nonmetals is well known. The solid-liquid interface in a melting or freezing metal can also be considered as a defect, in that there is a measurable difference in both sound velocity and density across the interface. For normal incidence of longitudinal waves in a typical case, about 10 percent of the pressure amplitude of the incident wave would be expected to be reflected. Thus such a technique could be considered as a method for measurement, feedback, and closed-loop process control in such applications as continuous casting of metals.

To examine the feasibility of this technique, the melting and freezing of 99.9 Sn has been studied at NBS using pulse-echo equipment at 5 MHz. The transducer contacts the cold end of a 5/16" x 8" specimen in a graphite mold in a Bridgman gradient furnace (unidirectional melting/solidification). Sharp echos easily locate the interface position, in both freezing and melting, to ± 1 mm, of the range of interface velocities tested (up to ~ 4 mm/min).

NBS work is focused on the study of the measurement factors inherent in possible use of the method for process control, as well as possible use for interface characterization. In those cases, such as continuous casting of steel, where signal/noise problems may be limiting, appropriate signal processing techniques should make it possible to improve signal/noise ratios. Applications of these techniques, including corrections for transducer response as well as signal averaging and correlation techniques, are being investigated.

To do this, a sampling oscilloscope is used to provide a slowed but shape-preserving output of the received echo, which is then fed to a digitizer and then to a small computer (64 k memory, Z-80 CPU, 8" floppy discs). With this set-up, using spatial averaging techniques, it has been possible to substantially improve the signal/noise ratio in specimens having large grain sizes that interfere, through grain scattering, with the signal observed from the back wall interface. Such grain scattering problems have been limiting in ultrasonic attempts to determine skin thickness in continuous casting of steel.

Solutal Convection during Solidification
Subtask 3 of Task 12143

S. R. Coriell, R. J. Schaefer

This research is directed toward an understanding of solutal convection caused by the simultaneous concentration and temperature gradients present during the directional solidification of alloys. Solutal convection affects the microstructure and chemical homogeneity of directionally solidified alloys, and hence essential properties and performance such as fracture and corrosion.

Previous theoretical work [S. R. Coriell, M. R. Cordes, W. J. Boettinger, and R. F. Sekerka, J. Crystal Growth 49, 13 (1980)] on solutal convection has shown that convective instabilities can occur at very low solute concentrations, e.g., 10 ppm for the solidification of lead alloys containing tin. Previous experimental work [W. J. Boettinger, F. S. Biancaniello, and S. R. Coriell, Met. Trans 12A, 321 (1981)] on the growth of lead-tin off-eutectic alloys has established that solutal convection can cause extensive macrosegregation and prevent the growth of aligned composites. Our present effort is to develop a detailed understanding of the fluid flow which occurs during directional solidification, and to develop predictive models for macrosegregation and solute redistribution.

For experimental study of convection during unidirectional solidification, we are using succinonitrile containing small additions of a lower density solute (ethanol). This material models the solidification behavior of metal alloys but since it is transparent allows direct observation of convection velocities. The physical properties of pure succinonitrile near its melting temperature (58 °C) are well known, but it was necessary to determine certain details of the succinonitrile-ethanol phase diagram. For measurement of the solidus curve, special procedures were developed for preparation of samples containing very low concentrations of ethanol and much lower concentrations of other impurities. Using the phase diagram characteristics thus obtained, calculations were carried out to determine the stability of solid-liquid interfaces during unidirectional upward solidification with respect to morphological and convective instabilities, as a function of ethanol concentration, solidification velocity,

and temperature gradient. The calculations indicate that the interesting transitions from stability to instability occur at concentrations of 10^{-3} to 10^{-2} weight percent ethanol and 1 to 10 μm/s solidification velocities. Although these are difficult conditions to work with, we have developed methods which make them attainable.

Convective flow is measured by photography of neutrally buoyant tracer particles dispersed in the solidifying material. Ideally, no convection would be present during unidirectional upward solidification of pure succinonitrile, but since strictly unidirectional heat flow cannot be attained in a real system it has been necessary to study the residual convective effects in pure succinonitrile to form a base line for comparison to solute-induced convection. The measurements of convective flow in the pure material have suggested several modifications of the unidirectional growth apparatus and of the convective flow measurement procedure which will reduce the background level of convection and increase the velocity range which can be studied by the photographic tracking method. These modifications are being made, and a test specimen for study of solute-induced convection in the concentration range of 10^{-3} to 10^{-2} percent ethanol is in preparation.

A theoretical effort in collaboration with Dr. R. G. Rehm of the Mathematical Analysis Division is developing numerical methods to calculate fluid flow and solute segregation during directional solidification. Such calculations should allow predictions of macrosegregation due to solutal convection during directional solidification as a function of the processing variables. In addition, the previously developed linear stability analysis is being extended to allow for flows parallel to the solid-liquid interface, and for solidification in the horizontal direction.

Surface Tensions and Their Variations with Temperature and Impurities Subtask 4 of Task 12143

S. C. Hardy

It has been widely recognized that surface tension measurements of liquid metals and semiconductors are flawed by the lack of any independent characterization of the chemical species present on the surfaces. Although modern surface spectroscopies would seem to provide a host of techniques which could address this problem, at least for some low vapor pressure materials, there have been hardly any studies of liquid surfaces by these methods. We have started a program of such measurements and recently have assembled an Auger electron spectrometer in which the liquid sample is studied in the form of a sessile drop so that surface tension measurements can be made in conjunction with the Auger analysis. Further sample characterization is provided by a video image of the surface formed by rastering the electron beam. The sample is mounted on a hot stage and the system is equipped with an ion gun so that samples can be cleaned by ion bombardment, a technique which we have found to be effective in eliminating solid surface impurities.

Our initial studies of liquid gallium have found the primary surface impurities to be oxygen and carbon. The oxygen is effectively removed by heating; the carbon, however, remains in the form of small platelets floating on the surface. Ion bombardment was used to remove these resulting in a surface free of impurities

within the sensitivity of the Auger analysis. The surface tension of gallium cleaned in this way varied linearly with temperature, a significant difference from the quadratic variation found previously for samples cleaned only by heating.

We have also studied the segregation of tin at the surface of gallium--1.9 percent tin drops by comparing the tin Auger line amplitudes with that of a pure tin sample. Although there is some uncertainty in the attenuation lengths and backscattering factors used in the analysis, surface concentrations in excess of two monolayers were found at 30 °C, with a sharp decline with increasing temperature. Surface concentrations calculated from surface tension measurements were in general agreement with this conclusion.

Diffusion-Induced Grain Boundary Migration
Subtask 5 of Task 12143

J. R. Manning, D. B. Butrymowicz, J. W. Cahn

Recently an unusual, totally unexpected phenomenon leading to very rapid alloying or leaching at low temperatures has been observed in a variety of materials. For example, in experiments done on this subtask, it has been found that zincification of copper and dezincification of α-brass can proceed at surprisingly fast rates in the temperature range 200 °C to 400 °C. These temperatures are much too low to allow any significant lattice diffusion through the interior of the alloy grains. Nevertheless a rather uniform addition or depletion of zinc in the interior of the grains is observed to occur, up to distances of several tens of microns from the surface. The process causing these surprising results, and similar results in other alloy systems measured at other laboratories and at NBS, can be shown to be diffusion-induced grain boundary migration. The relation of this migration to diffusion kinetics is being investigated.

In current NBS experiments, diffusion-induced grain boundary migration has been measured in CuZn, AuZn, and CuAs alloys. At the diffusion temperatures, which are less than half the melting point of the copper or gold foil specimens used in these experiments, only a negligible amount of diffusion occurs through the interiors of the grains. However, in the more open atom structures at the grain boundaries, a significant amount of diffusion still will occur. Thus, when Zn or As vapor was supplied from an alloy source and exposed to the pure Cu or Au foil, the Zn or As alloying elements could diffuse into the grain boundaries but not into the grains themselves. When the grain boundaries migrate, the regions traversed by the grain boundaries become alloyed with the Zn or As. It is found that a given grain boundary can migrate in one direction over part of its length but in the opposite direction over other parts. Also migration has been observed for both alloying and de-alloying. Thus, it has been proposed that kinetic processes, such as climb of grain boundary dislocations, rather than thermodynamic effects, are primarily responsible for the grain boundary migration.

Kinetic theories developed to explain this effect indicate a number of intriguing possibilities with significant practical implications. For example, in the steady state, the number of Zn atoms left behind in the region being traversed by the grain boundary should equal the number of new Zn atoms diffused

into the grain boundary from the vapor. In this steady state, a significant concentration gradient, producing steady state diffusion and grain boundary migration, might be maintained for appreciable periods of time. The resulting relatively large constant gradients in a moving boundary may be contrasted to those in a static grain boundary where the concentration gradients and hence diffusion fluxes normally decrease with the square root of time. This steady state with its effectively enhanced diffusion could sustain itself until the boundary has swept completely across the grain and produce large-scale surface alloy modifications important for wear and corrosion applications. Since this effects occurs only at low temperatures, perhaps less than half the melting point, high temperature processing may be avoided.

Diffusion in Metals Data
Subtask 6 of Task 12143

D. B. Butrymowicz, R. M. Hayes, J. R. Manning, M. E. Read

The phenomenon of solid state diffusion and its study has shed light on many problems of engineering, technological, and scientific importance. Diffusion in metals is intimately connected to the strength of metals at high temperatures, to metallurgical processes that are used to control alloy properties, corrosion of metals, and to many of the profound effects of nuclear radiation on materials. The NBS Diffusion in Metals Data Center provides a unique central source where data from the world's technical literature on diffusion and related kinetics are collected, evaluated, and then made available to the industrial and academic communities. More than 24,000 documents reporting diffusion data now comprise the Center's data base with many more arriving each month.

To cope with this influx (and to maintain the existing file) of data, automation of the Center's data base was initiated and, during the last year, a variety of data base management systems were reviewed and evaluated. The staff of the Center designed a customized management system that is able to create, maintain, update, and retrieve bibliographic and alloy classification data from the Center's data files. Approximately 4,000 documents have been prepared in computer-readable form. The Bibliographic Retrieval Services on-line system was engaged to provide operational needs. Concurrent with this automation activity were the initial steps of the in-house development of a data base management system for the Metallurgy Divison's computer to provide services for the Data Center's special needs. When completed, the automated bibliographic and classification data files will enable a quick response to inquiries from the technical and scientific community as well as make available camera-ready copy of such files.

A model system composed of data relating to copper and copper alloys is presently being constructed to test these automated services. This model system is an out-growth of a cooperative agreement between the Data Center and the copper industry's research arm, the International Copper Research Association, to provide critically evaluated data dealing with technologically important copper alloys. These data are also being published in handbook form as Volume VIII in the International Copper Research Association's Series on the Metallurgy of Copper. This volume is a companion volume to an earlier tome concerned with another group of copper-base alloys pertinent to research and development activities of this industry. This most recent volume is the culmination of a three-year effort funded by the Copper Research Association.

Efforts were initiated in the Data Center toward the collection and evaluation of transport data relating to critical, strategic metals. The Data Center has already within its data base a large fraction of the world's literature pertaining to these important materials. Evaluation activities are needed to yield reliable numerical values for diffusion and mass transport phenomena in these metals.

Metals Processing Laboratory
Subtask 7 of Task 12143

W. J. Boettinger, F. S. Biancaniello, S. D. Ridder, R. J. Schaefer, R. D. Shull

To accomodate research in the area of metallurgical processing, the activities of this laboratory are focused toward innovative metals processing technology. Particularly, several processing methods designed to produce rapidly solidified powder, continuous filament and surface layers are being used to determine the processing-microstructure-properties relationship. Rapidly solidified powders are being produced by an electrohydrodynamic method which forms and ejects small quantities of extremely fine (< 10 μm diameter) molten alloy droplets. The droplets solidify in flight, and due to large undercoolings attained prior to solidification, contain a wide variety of microstructures. A major advantage to the method is that the particles are often electron transparent, a fact which simplifies characterization. Also under investigation for powder production is a technique using a Laval tube. This technique, which previously has been used for commercial production of kaolin fibers, makes use of the simultaneous flow of molten metal and gas through a tube with a shape designed to create a rapid expansion. This expansion breaks the liquid metal into droplets. The extension of this technique from ceramics to alloys is under way.

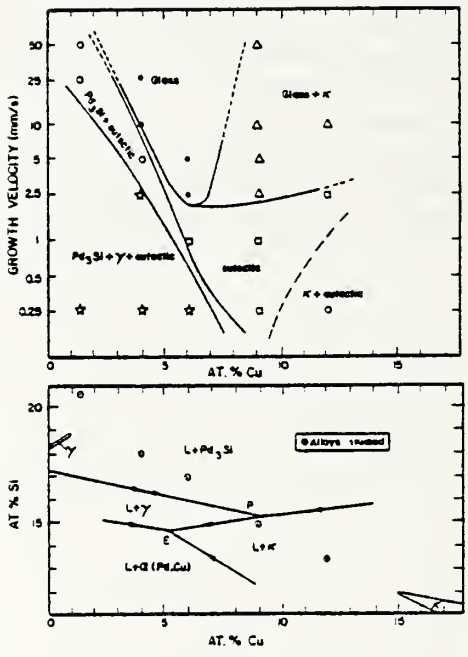
A vacuum melt spinning device has been constructed to produce ribbons of metallic alloys cooled from the liquid at rates approaching 100,000 degrees per second. Such fast liquid quenching allows for the creation of bulk metallic glasses and metastable crystalline alloys, and investigations of their morphology and structure are presently being conducted.

Electron beam surface melting is being used to produce rapidly solidified surface layers. These layers are used both for the study of the effect of rapid solidification on microstructure and for wear and abrasion studies. The scanning and pulsing capabilities of the electron beam melter have been upgraded and thoroughly characterized, and new methods have been developed for measuring the electron beam energy profile. As a result, this instrument can now be used for quantitative surface melting experiments in which microstructures are correlated to computed solidification velocities. Several different scanning modes can be used to obtain samples suitable for a variety of different studies.

Research in the area of macrosegregation occurring during the continuous and electro-slag remelting of ingots also is being performed. These studies involve the use of a small-scale casting apparatus capable of producing ingots up to 90 mm in diameter and several hundred millimeters in length. The ingot molds can be cooled with water or oil pumped from temperature controlled reservoirs allowing precise control of cooling rates and casting speeds. A series of thermocouples placed in the ingots as they are cast provide both

radial and axial temperature profiles. This information is used to compare theoretical calculations of macrosegregation to those measured in the experimental castings and, therefore, test the accuracy of the proposed mechanisms of macrosegregation in these casting processes. Presently the macrosegregation present in commercially produced continuous cast ingots of 2219 and 2024 aluminum alloys has been characterized. Special reduced cross-section ingots have been laboratory cast to simulate varying degrees of macrosegregation in these commercial alloys.

Finally a major output of the laboratory is data regarding the heat treatment of wrought aluminum alloys. The purpose of this research is to determine the "quench sensitivity" of two aluminum alloys, 2219 and 2024. A complete series of heat treatments has been conducted for these alloys which determine the effects on microstructure, mechanical properties and NDE response due to interrupted or slack quenching from solution heat treatment temperature. Such studies have been greatly streamlined with a data acquisition system which records temperature-time data for each heat treatment and permits direct data flow to algorithms used to produce isothermal TTT curves.



(a)

(b)

Fig. 1. (a) Summary of the effect of growth rate and composition on the microstructure of Pd-Cu-Si alloy. (b) Alloy compositions used in these studies are plotted on the liquidus surface.

MECHANICAL PROPERTIES AND WEAR
Task 12144

This task addresses the measurement and standards needs concerned with the application of metals to wearing situations, and also to their use as synthetic implants in humans. Principal emphasis in the various projects described below concerns the effects of metallurgical parameters, the need for better understanding of basic mechanisms involved, and the issue of better measurement methodology including the development of standards and reference materials.

The importance of wear to U.S. industry and technology has only been appreciated fully in recent years. Studies indicating the costs of wear have been conducted in three countries (U.S. costs are estimated at $30B to $50B per year) and those results have led to increased Government and private emphasis of wear control and wear research. Most of the work in this task resulted from an expanded NBS program in FY80 through the Durability Initiative. NBS has a unique opportunity in this field to provide help to the industry in standards and measurements areas, as well as to contribute to an improved basic understanding of wear. One area of current industrial interest involves coatings applied to metals for improved wear (and corrosion) performance. More widespread use of coating technology can conserve critical materials (by reducing their use in bulk alloys) and can improve productivity by efficient use and reuse of existing designs and components. However, the state of understanding of wear of thin metal coatings is not well advanced. Methods for accurate wear testing of very thin coatings are not adequate. These and other related needs are important technological questions for NBS to address in the wear area; in fact, a proposed budget initiative for FY82 includes work on the wear performance of metals coatings.

Highlights of this year's achievements include the development of a new galling wear test system, studies of the wear of nickel alloy coatings, development of a standard reference material for abrasive wear testing, and results on the break-in wear of copper alloys. A very successful International Wear Conference was held this year to which our staff contributed three papers and served as Program Chairman. We also hosted a successful ASTM Symposium on Fretting Wear at the NBS laboratories this summer.

The work in this task on metallic implant materials contributes to a special but very important area of technology. Each year millions of people benefit from either permanently or temporarily installed metallic surgical implants. As technology advances, improvements are made in implant materials and in determining reactions of the body to them. In this past year task members conducted research on properties and performance of a number of implant alloys. Special emphasis was placed on cobalt-chromium-molybdenum alloys and titanium alloys, and on the effects of processing variables on performance. The interest of the technical community, industry, and implant users is evidenced by the large number of requests received by task members for papers, talks, and data. In addition to scientific studies, standards work and meeting organization activities are an important part of this task. The proceedings from the NBS Conference on "Implant Retrieval: Material and Biological Analysis" was published this year and more than 500 copies mailed out. Implant standards meetings have been held involving our staff and another is planned with the Society for Biomaterials. Significant contributions also were made to the ASTM F4 Committee on Medical and Surgical Materials Devices.

The task is divided into four subtasks whose activities and accomplishments over the past year are described next. These subtasks are Mechanisms of Metallic Wear, Lubricated Wear, Wear Standardization and NDE, and Metallic Biological Implant Materials.

Mechanisms of Metallic Wear
Subtask 1 of Task 12144

K. J. Bhansali, P. J. Blau, L. K. Ives, F. Matanzo, A. W. Ruff

This subtask is concerned with friction and wear behavior of a number of metals and alloys under conditions of clean, dry sliding, and under abrasive and erosive conditions. The emphasis is on precise, meaningful measurement of wear and friction and on improving the understanding of basic wear mechanisms, particularly the role of metallurgical parameters. Wear tests are carried out in the laboratory under carefully controlled conditions and are designed to explore particular aspects of the usually complicated wear process. Electron microscope methods and surface analysis methods are emphasized in gathering information and data.

Investigations of the variations in friction coefficient and wear rates during dry sliding have been conducted using Cu, Cu-3.5 wt % Al, and Cu-7 wt % Al alloys. Polished flats of these materials were slid against rotating rings of 52100 steel in argon. A mini-computer controlled the tests and periodically recorded friction forces and specimen displacements. Calculated friction coefficients were plotted as a function of time to examine the nature of running-in friction transients. These data were examined in light of surface and subsurface microstructural alterations due to sliding. Running-in behavior of sliding couples using worn and unworn 52100 steel rings as the initial counterfaces showed distinct differences. These studies of initial friction behavior may help to identify dominant surface processes as they develop to reach a steady state sliding condition. Plans for the coming year include studying some more complex Cu-Al commercial bearing alloys for running-in behavior. The evidence for various microstructural mechanisms, particularly metal transfer to and from the counterface, will be compared with that previously observed on the Cu-Al research alloys.

In another project activity, a linear, stroke-by-stroke, ball-on-flat tribometer was used to analyze the break-in friction behavior of an Al-Si alloy. This alloy is typical of those currently used in engine blocks of certain automobiles and power chain saws. The tests were computer controlled to permit measurements of friction forces at specified locations on the sliding wear track. Tests were conducted under dry conditions using 52100 steel balls as sliders. Polished surfaces were found to produce quite different break-in results compared to etched surfaces which had harder Si particles standing above the matrix aluminum phase. Tests were also run on both pure Si and 2024 Al alloy flats to compare with the behavior of the more complex Al-Si composite material. Microstructural observations with optical and scanning electron microscopes were combined with computer-plotted friction data to serve as a basis for a new model of composite wear-in. This model involves surface microfracture of Si particles, Al matrix transfer to the slider, slider deformation, wear debris in-filling, and subsurface pre-fracture of Si particles which emerge at the wear surface already cracked. This model explains several features of the changes of friction coefficient during the break-in period.

Studies of the effect of plastic ductility and tensile strength of a series of steels on their wear behavior are continuing. Three additional HSLA steels are being studied. They vary in both mechanical properties and chemical composition. When completed, this study of five steels will permit a comparison of their dry sliding wear behavior with various mechanical properties, particularly plastic ductility. It is thought that wear particle formation under these conditions is determined by plastic ductility, and therefore controlling of wear rate. In addition the depth and structure of the deformed zone beneath the worn surface will be determined and compared with wear debris size and bulk mechanical properties.

Another project has studied the wear of a series of Ni-P alloy deposited coatings on tool steel under dry sliding conditions. This work, done jointly with Dr. Lashmore in the Chemical Stability and Corrosion Division, studied the effect of different phosphorous content, heat treatment, and compared amorphous and crystalline electrodeposited coatings. It was found that a laminar microstructure existed in all the Ni-P coatings studied, and this affected the wear behavior. The wear rate for the amorphous Ni-12P coating was about one-half that of the crystalline coating. An electroless Ni-5P alloy proved to be the most wear resistant deposit studied. These results will be presented in the fall at an ASTM symposium on wear testing of coatings.

Construction of a wear tester to study the mechanisms of galling and scuffing wear has been completed. The test unit is capable of loading engineering and research alloys up to plastic yielding. A project to study the influence of basic materials properties on galling and scuffing wear has been initiated. Preliminary tests on engineering alloys like mild steel, 2024 aluminum, copper, and brass have been conducted. In alloys with high stacking fault energies like aluminum and copper, galling is observed at applied loads corresponding to 10 to 20 percent of their yield strength. Addition of 30 percent zinc to copper results in an alloy (70-30 brass) with lower stacking fault energy than copper. No galling has been observed so far in this alloy up to 60 percent of its yield stress, confirming similar findings reported earlier in nickel- and cobalt-base alloys. In the next phase, a set of alloys with controlled variation in stacking fault energy will be made and studied with this test in order to explore the effect on galling threshold stress.

Abrasive wear of lightweight composite aluminum alloys has been studied in a project supported by the U.S. Army Materials and Mechanics Research Center. The dry sand/rubber wheel method was used in this study. Composites of aluminum matrix with alumina particles showed an improvement in wear resistance over that of the matrix compositions alone by a factor of two while retaining most of the mechanical properties. Aluminum composites containing silicon carbides, on the other hand, lacked the necessary interfacial strength to cause any improvement in wear resistance. In the next project phase, composites of aluminum alloys with particles of chromium carbide and titanium carbide will be made by surface alloying methods in the hope of achieving better interfacial bond between the hard carbides and soft aluminum matrix.

The recently purchased wet sand abrasive wear test machine has been set up and run. This machine will provide a second method for studying metal abrasion using various wet environments. The pivot block was modified to center the wear scar and the specimen holder redesigned to facilitate mounting and removal

of 74 mm (3 inch) long specimens, the size used in the dry sand test. Fixtures have been machined to permit calibrating the actual load on the specimen. A one hp variable speed electric motor and control unit have been obtained to replace the existing fixed speed motor to provide more flexibility in studying wet abrasion of metals. A number of the metal composites will be studied using this wet sand abrasion system.

A project studying the abrasive wear properties of laser surface melted, particulate strengthened aluminum and titanium alloys has continued this year. Specimens have been made at the Naval Research Laboratory in this cooperative study using a laser melting system modified so that particles of WC and TiC can be blown into the molten pool at the laser beam location. After the entire surface is scanned, a rapidly solidified layer containing up to 50 vol % of hard phase particulates and up to 1 mm deep is produced. Abrasive wear measurements were carried out on these specimens using the dry sand/rubber wheel method. Improvements in the wear resistance of up to a factor of 10 were found to result from this surface modification treatment. Studies of the effect of particle size, spacing, type, alloy composition, and microstructure have been carried out. Analysis of the effects of these parameters on the wear rate is being conducted.

Lubricated Wear
Subtask 2 of Task 12144

L. K. Ives, M. Peterson, A. W. Ruff

The purpose of this project is to develop and evaluate bench wear tests to be utilized for the characterization of rerefined engine oils. Support is provided by the NBS Recycled Oil Program which was established in response to the Energy Policy and Conservation Act of 1975. That Act directs NBS to develop tests which determine the substantial equivalency of recycled oils to virgin base oils. A particular wear test method, the Suntech-Timken method, has shown promise in our work and has been the subject of an intensive study during the past year. The test is similar to an existing ASTM wear test method, D2782, and employs standard ASTM ring and block specimens. A given oil is character-ized by determining the load range within which scuffing or galling occurs. In this regard the Suntech-Timken method is similar to numerous existing tests, including several ASTM tests. However, the Suntech-Timken method differs from most in that a very limited quantity of oil (about 0.2 ml) is employed. During the course of a test, loss of lubricating ability may occur as a result of a combination of thermal effects, oxidation, and adverse reaction with the metal surface. Thus, not only is the capacity of fresh oil to prevent severe wear measured but also the ability of the oil to resist degradation of properties is determined. The Suntech-Timken method has been applied to a series of ASTM IIID engine sequence test oils and its validity was demonstrated by properly ranking these oils according to their known engine wear characteristics. Furthermore, application of these reference oils has served to provide an absolute calibration of the test. An investigation of the additive response characteristics of several rerefined base oils also has been carried out sucessfully. In addition, tests are being conducted on rerefined motor oils that have been the subject of a field test program in vehicles operated by the Royal Canadian Mounted Police Force. Results obtained with these oils will further delineate the ability of the Suntech-Timken

method to correlate with certain apsects of the service performance of motor oils, rerefined motor oils in particular. A final report providing a detailed description of the Suntech-Timken method and all the validation results is being prepared this year.

Another project concerns the need by the Navy for improved lubricants for application in severe environments, and to metals such as stainless steels that are difficult to lubricate. Lubricants having extended lifetimes are also needed to reduce costs by increasing intervals between maintenance. The Navy has sponsored industrial development of several potentially effective new solid lubricant materials. One of the most promising of these is Sb_2S_4. We have received project support from the Office of Naval Research to carry out an in-depth study of the lubricating characteristics of this material and other related solid lubricant compounds. Our program has two components: (1) to determine the basic mechanisms(s) by which Sb_2S_4 behaves as a lubricant, and (2) to determine its effectiveness in preventing wear of various metal bearing materials under selected contact conditions and environments. Considerable progress has been made during the past year on the first component of this program. Studies have been carried out on Sb_2S_4 in the dry powder form and when added to lubricating greases and oils. Sb_2S_4 is amorphous in structure and therefore, in the absence of a phase transformation during wear, does not behave like such well known layer-lattice lubricants as MoS_2 and graphite. Indeed, sliding wear tests conducted on the powder indicate that Sb_2S_4 is at best a poor dry lubricant. At elevated temperatures a reduction in friction coefficient is observed at about 220 °C but the improvement is marginal. When added to a grease, however, Sb_2S_4 confers a significant improvement in load carrying capacity--equal to or better than the best organic additives--as determined in 4-ball tests, and pin/V-block tests. Analysis of wear debris and residual lubricant materials by means of electron diffraction has revealed that Sb_2S_4 provides sulfur to the metal surface as a consequence of the decomposition of Sb_2S_4 to Sb_2S_3. This leads to the formation of metal sulfide films on the surface. Thus, presently available data indicate that Sb_2S_4 functions mainly as a chemical additive. The extent of any additional physical effect is still being investigated. Other investigations are being carried out to determine the long term wear behavior of Sb_2S_4 in grease on several metal combinations. Studies are also planned utilizing surface analytical methods and transmission electron microscopy to analyze the films produced on worn surfaces.

Wear Standardization and NDE
Subtask 3 of Task 12144

P. J. Blau, L. K. Ives, F. Matanzo, A. W. Ruff

This project is concerned with improving an abrasive wear test that is widely used in industry. It has been estimated that perhaps 50 percent of all wear can be traced to abrasion. Excavating, mining, and agricultural machinery as well as a variety of equipment used in processing and handling abrasive material must be designed to minimize abrasive wear damage. Accurate data and appropriate test procedures are necessary both for equipment design purposes and to assist in the development of more economical and improved materials. The ASTM standard dry sand/rubber wheel abrasive wear test (G65-80) is found to yield results that correlate well with service behavior when the stresses imposed on abrasive

particles are relatively small. Project staff members have made significant contributions to the development of this standard test and participated in several interlaboratory test series.

The value of the standard dry sand/rubber wheel abrasive wear test method depends critically on an appropriate calibration procedure. Calibration is best accomplished through the use of reference specimens having consistent and well established wear behavior. With the support of the NBS Office of Standard Reference Materials reference specimens of D-2 tool steel have been developed and are ready for issue. The specimen material was selected on the basis of our own studies and recommendations of ASTM G-2 Committee members employing the dry sand/rubber wheel test. The reference specimens will be sold by NBS this fall in sets of three for use in standardizing this test. The possibility of developing additional reference wear test materials having higher and lower wear resistance than D-2 tool steel is currently under study.

The project to develop standard reference materials for the dry sand/rubber wheel test has also included an extensive investigation of the effects of various machine test parameters and conditions. Abrasive wear data gathered during the past year concerning test variable effects have been analyzed and tentative conclusions have been reported in a draft report. Gaps in the information and questionable data will be the subject of future tests, including the effect of the lapse time or test order, moisture content of the sand, and sand flow rate. The machine is now operating with an arm that incorporates a load cell to measure the friction force. An infrared sensor is also in use to measure the surface temperature of the rubber rim. Both of these measured test parameters are being recorded on a dual channel recorder. To increase data recording and analysis capabilities an eight channel digital recorder is being made ready for operation.

Quantitative image analysis is being employed in another project to develop meaningful sand particle shape parameters which relate to their abrasiveness. This project, sponsored by the Office of Standard Reference Materials, is focused on characterizing the abrasive specified for the ASTM Dry Sand/Rubber Wheel Abrasion test. Abrasive shape has been shown to greatly affect abrasive wear and a more quantitative measure for particle shape could result in improved reproducibility. The goal of this study is to produce a standard method to characterize shape, and a series of particle shape standards for calibrating conventional image analyzing equipment. During the past year a perimeter ratio method was seen to discriminate between sands with three different origins: foundary sand, beach sand, and crushed quartz. Future work involves exploring the variability of the perimeter ratio among batches of foundary sand, studying instrumental limitations for measuring perimeter ratios, and generating sampling requirements to obtain statistically significant values of the shape parameters.

Another standards related project concerns the use of Knoop and Vickers diamond indentation microhardness tests for measurement of the hardness of small, selected areas on metal surfaces. Hardness values are calculated from the sizes of the indentations produced with specified loads on the indenter. The equations used to calculate microhardness numbers assume that the unloaded impression shapes duplicate the indenter shape, but studies with Knoop indentations (elongated diamond shape) show that this assumption usually is not

valid. Shapes of impressions may be affected by the microstructural characteristics of the test piece (e.g., crystallographic orientation, residual strains from surface preparation, etc.). An investigation of Knoop impression variability in metals of different microstructures was conducted. One amorphous alloy (Pd-Cu-Si) was examined to see if its high degree of uniformity would lead to less microhardness indentation shape variability. Plans for the coming year include the investigation of electron beam surface melted tool steels as potential microhardness standard materials. The work is proposed for sponsorship by the Office of Standard Reference Materials.

In a project concerned with solid particle impingement erosion of metals, another round of interlaboratory measurement comparison has been completed through the ASTM Committee G2. NBS provided specimens and the test protocol to five other labs in this activity. A draft standard of the test method developed here was also balloted through the sub-committee. The results of the test were very encouraging; typical within-lab precision was 10 percent, between-lab precision about 40 percent, due apparently to biases in measuring particle velocity. Normalization using a reference material should remove this problem. One additional round is planned this fall under different experimental conditions; this should finalize the necessary steps to complete the entire standardization processs. This standard permits solid particle erosion measurement of metals under specified laboratory conditions for the purpose of preliminary screening and alloy development in the industry.

A project concerned with nondestructive evaluation of the condition of wearing systems has continued. Emphasis has been on the standardization of wear debris analysis and on the use of acoustic emission to detect major wearing events such as microcracking. We have worked with a group of six other laboratories in a Navy-sponsored program to standardize the ferrographic method of wear debris analysis. We have produced a collection of wear debris particles using two wear test methods that served as one type of test specimen material of debris in oil; two other types of debris/oil collections were furnished by other participants. An agreed upon standard method of analysis was used (this method is now being considered by an SAE standards committee for approval). The results of comparative measurements indicated precision within a typical lab of about 10 percent and agreement between labs of about 40 percent. The principal source of systematic bias remaining was clearly the microdensitometer used to measure wear particle density on the deposit slide. We have proposed two reference materials to help solve this problem: one is a graded density slide to calibrate the optical density measuring system; the other involves photographic duplicates of a typical debris particle deposit for use in validating the entire reader system. If successful, these reference materials could reduce the total variability to 15 percent or less. This would greatly facilitate interlab comparisons of wear rates in operating systems and should further the application of this wear monitoring approach. Preliminary studies of acoustic emission from a sliding wear (block/ring) test have continued. A search is underway for the most suitable wear geometry and choice of metal in order to maximize the chance for success in detecting microcracking during wear. The amplifier and video recorder system we plan to use appears to have adequate sensitivity and band width. Experiments are planned yet this year to study a low toughness steel and a two-phase aluminum alloy.

It is planned to attempt to relate wear rate and subsurface damage to the acoustic emission events.

Metallic Biological Implant Materials
Subtask 4 of Task 12144

A. C. Fraker, J. S. Harris, G. J. Mattamal, A. C. Van Orden

This is a continuing project which involves the study of mechanical and chemical behavior of metals and alloys which are used as surgical implants. Changes and improvements in implant metals occur as new alloys are introduced, currently used alloys are modified, and combined materials (metal, ceramic, polymer) are used. Due to this interest in new materials and developments, much property data and characterization information are needed. This project has conducted extensive work on implant metals in the areas of corrosion-fatigue, corrosion, metal/protein interactions, and surface preparation. Collaborations with several guest workers bring to the project additional expertise in electrochemistry, metal alloys, mechanical properties, and stress evaluation. Dr. Pei Sung from the Bureau of Medical Devices, Food and Drug Administration, and Dr. M. Ashraf Imam from the George Washington University participate in this project as guest workers. Dr. Kirk J. Bundy of Johns Hopkins University is a contractor this year. A new study in this project is an investigation supported by the Food and Drug Administration to determine the influence of metal surface preparation on the bonding of bone cement in prosthesis applications (e.g., hip joints). Surface films have been analyzed, a literature survey completed and mechanical tests to determine bond strength are getting under way.

Titanium alloys are being used increasingly for surgical implants. In addition to analyzing surface films and corrosion behavior of titanium alloys, the project collaborates with scientists at George Washington University to study the influence of heat treatment and resulting microstructure on the corrosion-fatigue life. Transmission electron microscopy is used for detailed microstructural analysis. Fatigue behavior of implant alloys is an important aspect of their eventual application. Two alloys studied were Ti-6Al-4V (which is currently used for surgical implants) and Ti-4.5Al-5Mo-1.5Cr (Corona 5). Data were obtained to show the influence of heat treating and microstructure on corrosion-fatigue life for both these alloys. Results indicate that at lower strain levels, the Corona-5 alloy has a longer corrosion-fatigue life than Ti-6Al-4V while the opposite is true for higher strains. More data are needed on effects of heat treatment of both alloys. Some of these results were presented at the Conference on Titanium in Phoenix, Arizona, April, 1981. Other corrosion-fatigue studies have dealt with the cobalt-chromium-molybdenum alloy in three conditions: cast, forged high strength, and hot isostatically pressed. Torsional fatigue tests are conducted under fully reversed torsion at a constant shear strain amplitude and frequency in a flowing physiological saline solution at 37 °C. Test results on the cobalt-chromium alloy in the forged high strength and hot isostatically pressed conditions show significant improvement over the cast material especially in the low cycle to failure range but also in the high cycle to failure region. These results were presented at the Society for Biomaterials Meeting, Troy, New York, May 1981. Tensile loaded corrosion fatigue tests using a new servo-hydraulic machine also are in progress to study the fatigue strength of implant metals. An environmental test cell was designed and built for this system, which will use an ASTM recommended test specimen. Tests are being conducted under a constant amplitude and frequency in a flowing physiological saline solution at 37 °C. A scanning electron microscope study of the fatigue specimens from both types of fatigue tests is being conducted to give insight to the complex relationship between failure mode, environment, and microstructure.

Anodic polarization measurements in physiological solutions are used to determine effects of environment and chemical composition on the corrosion behavior of implant alloys. Anodic polarization tests have been conducted on Ti-4Al-5Mo-1.5Cr to determine effects of cysteine, an amino acid containing a sulfhydril ion. The addition of the cysteine was shown to result in increased current density but did not significantly affect the breakdown potential of the metal. Significant progress also was made this year in the study of several cobalt-chromium alloys. A series of anodic polarization tests was run in physiological saline solution on four Co-Cr alloys: cast, and forged high strength (three compositions). The emphasis of these tests was to determine the effect of variations of the amount of Fe present in the FHS form of the alloy and the effects of differences in processing treatments. Following anodic polarization tests, the surface films were analyzed using light microscopy, scanning electron microscopy, and energy dispersive x-ray analysis. The SEM and EDX analyses showed significant differences in the thickness and compositons of the films; the alloy containing the most Fe produced the thickest and most Fe-rich film. A report of this study is being prepared for publication.

A collaborative effort with Dr. Pei Sung of the FDA deals with alloy surface film formation and stability in saline solutions. These studies show that all metals used as implants do repassivate readily but surface film stability varies widely with increasing voltage. The study is comparing the implant metals and the effect of various surface modification treatments.

Metal/protein interactions are being investigated. The approach used is to determine the amount of metal ions which attach to human blood serum albumin (HBA) by means of ultrafiltration and atomic absorption techniques. Emphasis this past year has been on analyzing bound chromium and nickel which were introduced to a 1 percent HBA solution electrochemically and by salt addition, respectively. Binding did occur in both cases; data are still being collected to confirm results. An atomic absorption apparatus has been used for this purpose. It is anticipated that in the future potentiometric titration methods and other techniques will be used in this study. The nickel ion is being investigated currently by using 5 ppm to 600 ppm (0.1 to 10 mM) in the form of $NiCl_2$. The relation of pH to binding is also being considered.

Standards for biomaterials and test methods are promoted as part of this project. Leadership in standards work is provided to the Society for Biomaterials by chairing the Standards Committee. A meeting on the "Status and Needs of Standards for Biomaterials" was organized and held at the annual meeting this year. This meeting was well attended and another is planned for next year. Other standards work of this project occurs in the ASTM F-4 Committee on Medical Materials and Devices. Changes in existing implant metals and the introduction of new metals requires effective standards and specifications. This project contributed electrochemical data on the widely used cobalt-chromium-molybdenum alloys to the ASTM for use in discussing the significance of small composition variations in setting specifications.

This project has participated in interlaboratory tests for a method to determine pitting and crevice corrosion resistance of implant metals. This test method is at the final stage of ASTM balloting and its acceptance will necessitate the development of standard reference materials. Two series of pitting and crevice corrosion tests were conducted for the ASTM interlaboratory test

program. Both tests were run on 316 L stainless steel in a 0.9 percent NaCl solution. In the second series of tests the passivation treatment used for implant metals was added to the procedure. Participation in the ASTM interlaboratory tests will continue with some refining of the tests to evaluate the influence of experimental parameters such as solution pH, oxygen content, and metal passivation treatments. Preparation and testing will be done for the production of standard reference materials. This work is partially funded by the Office of Standard Reference Materials.

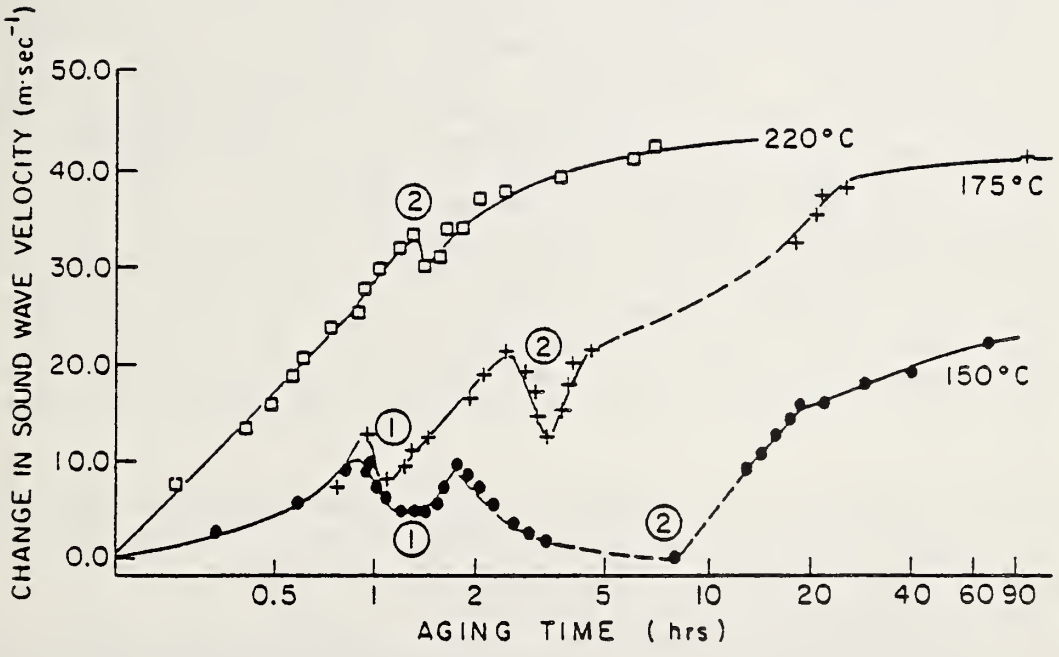


Figure 1. Change in ultrasonic sound wave velocity as a function of aging time at three different temperatures in 2219 aluminum alloy.

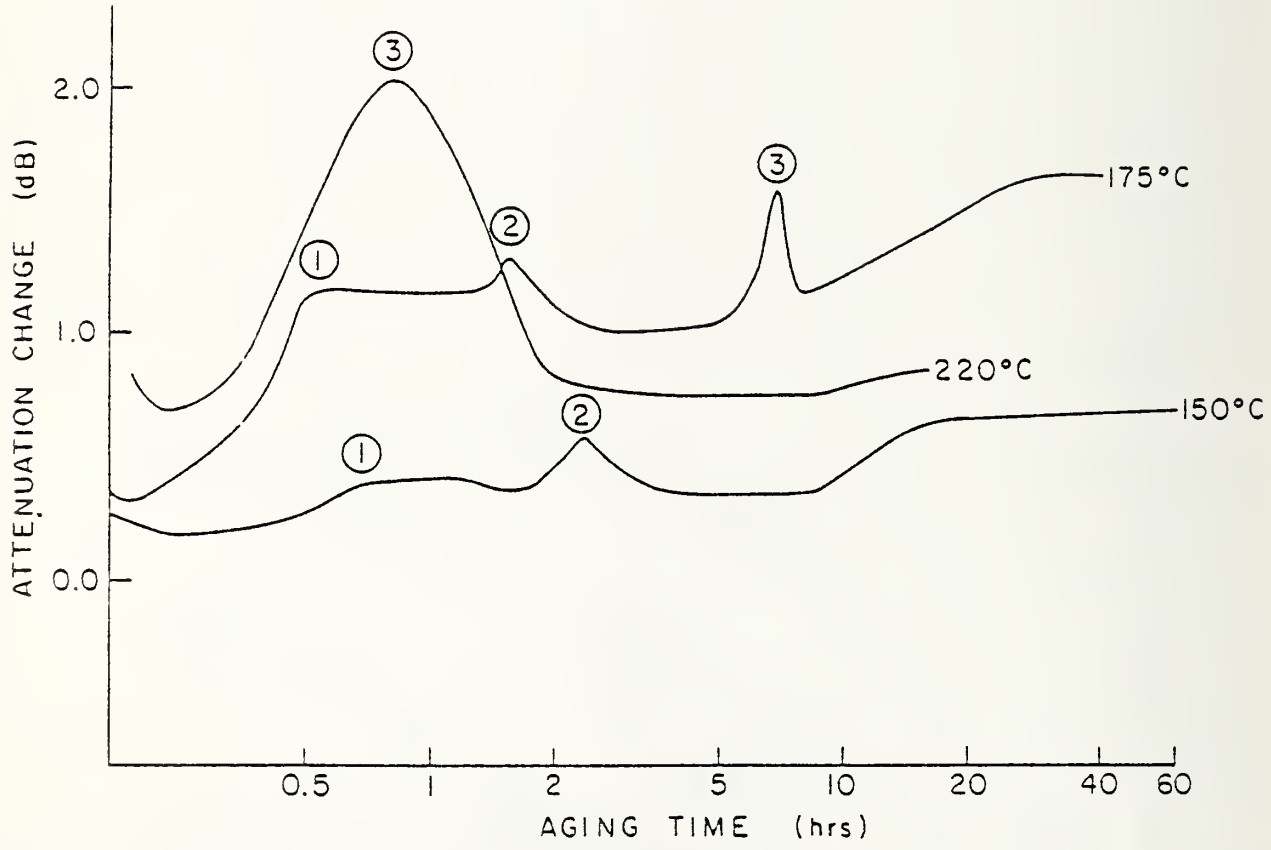


Figure 2. Change in ultrasonic sound wave attenuation as a function of aging time at three different temperatures in 2219 aluminum alloy.

CHEMICAL METALLURGY
Task 12145

The interplay between thermodynamic predictive models and the formation and stability of alloy phases is the central theme of this task's activities. This theme is developed in data, theory, and experiment. Conventional and new experimental techniques are combined with theoretical models in the determination and prediction of phase diagrams. Special emphasis is placed on the development of on-line computer graphic systems. In addition to its fundamental scientific interest, advancement in the understanding of phase diagrams is essential to permit greater flexibililty in development of new alloys for improved performance, ease of processing, reduced cost, and energy use, as well as in providing substitutes for scarce elemental additions.

The joint effort mandated by agreement between the Directors of the National Bureau of Standards and the American Society for Metals (ASM) has continued to provide critically evaluated phase diagram and other constitution data as well as related bibliographic material. Technical oversight of this program and work on selected systems is being carried out by the Alloy Phase Diagram Data Center (supported in part under this task and by the Office of Standard Reference Data). ASM continues to support a Research Associate at NBS for this project and has initiated a $4M fund-raising effort from industry. A quarterly Bulletin of Alloy Phase Diagrams is also published under this program. A major new effort was also initiated as part of this program to evaluate all binary titanium alloy phase diagrams. The project of compiling and evaluating phase diagram data for all binary titanium systems has three aspects: (1) to provide accurate phase stability information on titanium alloys, (2) the titanium category will serve as a model for the rest of the categories in the NBS/ASM joint program on binary phase diagrams, and (3) to create a modern computer-based phase stability data compilation. The program has four basic and interrelated components. These include compilation and evaluation, development of bibliographic methods, thermodynamic optimization, and development of computer software.

Experimental phase diagram work has been concerned with the binary and ternary systems relevant to the Ti and Al rich corner of the quinary system Ti-Al-Mo-Nb-Ta. This work is being done with the partial support of the Navy. The Ti alloys involved in this system have important present and potential practical advantages. Their high corrosion resistance makes them attractive for marine and chemical processing applications and their high strength-to-weight ratio makes them valuable in aviation and space technology.

Other activities in this task include theoretical work on understanding parameters important to alloy phase stability, completion of our DOE-DOD fuel cell catalyst program, and a major effort in the evaluation of possible nonuniformities in two aluminum alloys used by NASA in the Space Shuttle. The latter program, while reported under this task, has involved many of the scientists in the other groups in the Metallurgy Division.

Alloy Phase Stability
Subtask 1 of Task 12145

L. H. Bennett, J. R. Cuthill, D. J. Kahan, J. L. Murray, L. J. Swartzendruber, R. D. Shull

We are pursuing a program of three interconnected parts: critical evaluation and compilation of binary phase diagram data, experimental work on phase stability on alloy systems selected with a view to complementing the evaluation program, and the theory of phase stability, stressing the prediction of the heat of formation of transition metal binary alloys.

Alloy Phase Diagram Data Center Activities. Alloy Phase Diagram Data Center activities revolve about a collaborative alloy phase diagram critical evaluation program with the American Society for Metals (ASM). This program now is active in the preparation and dissemination of a comprehensive computer-accessible data base of binary and multicomponent alloy phase stability data. The data which are to become accessible by computer include not only the graphical phase diagrams themselves, but relevant metastable equilibria and thermodynamic properties, an annotated bibliographic data base, and the text of the evaluation. In order to carry out the critical evaluation of data, an International Council of experts in thermodynamics and phase stability acts as advisors on the scope and format of the evaluations, supported by additional panels of experts dealing separately with binary and multi-component systems. The actual evaluation of the phase diagram data is being carried out throughout the world at institutions with special expertise in certain alloy systems. Prof. T. B. Massalski, as Chairman of the Panel on Binary Alloys, has recently completed a one year visit to NBS. One of the results of his work has been the appointment of category editors for the binary systems of: Ti, Cu, Ag, V, Cd and Zn, alkali metals, rare earths, and the actinides.

The first three issues of the Bulletin of Alloy Phase Diagrams have appeared. This Bulletin, edited at NBS and published by ASM, is the main method of rapid dissemination of evaluated phase diagrams produced by category editors. The Bulletin also has acted as a vehicle for open review, and feedback comments have been published. Articles have appeared listing crystallization temperatures for metallic glasses, and providing a thermodynamic basis for understanding phase diagram features and transformations of metastable phases.

At NBS a model category is being evaluated in order to establish criteria for critical phase diagram evaluation ("standards of evaluation"). In this connection, Joanne Murray is category editor for Titanium. The first eight systems (Ti-Zr, -Hf, -V, -Nb, -Ta, -Cr, -Mo, and -W) have been completed for publication in the Bulletin of Alloy Phases and also have been compiled in report form. The systems Ti-Mn, -Fe, -Tc, and -Re are in preparation for publication, and the systems Ti-Co, -Os, and -Ru are being evaluated now. This work is serving to define the scope and organization of phase stability data, to provide a role for thermodynamic modeling in both the evaluation of data and the creation of accurate graphical diagrams. It also has stimulated the development of the computer tools required for the establishment of a computer data base organized on sound metallurgical principles.

NBS has available a computer program for the on-line graphical display of phase data which produces camera-ready, publication-quality binary and ternary phase diagrams, and a separate program to calculate and optimize phase diagrams from thermodynamic data. Progress has been made this year in interfacing these programs with each other and in making them efficiently accessible to the user. It is possible now in a single interactive computer session to calculate a phase diagram, compare it graphically with the experimental data on which is it based, and create permanent computer files of both the user output and the fundamental data. Because many systems have now been computerized, the current task is to create the machinery to handle an archive of such files. Work is underway now to create a central program-independent format for all the phase diagram data (including, for example, bibliographic data) and to write a package of the several programs needed to create, update, document, or publish these files.

We have advised ASM in the preparation of an on-line phase stability bibliography by developing the search strategy used to separate phase diagram literature from the METADEX system. The results of the search are being set up now as a database at BRS (Bibliographic Retrieval Service). In addition machine readable bibliographies have been compiled at NBS in conjunction with the Ti evaluation, and these will be used to complete the partial data base taken from the METADEX search.

Experimental Phase Diagram Program. Experimental phase diagram work has been concerned with the binary and ternary systems relevant to the Ti and Al rich corner of the quinary system Ti-Al-Mo-Nb-Ta. This work is being done with the partial support of the Navy. The Ti alloys involved in this system have important present and potential practical advantages. Their high corrosion resistance makes them attractive for marine and chemical processing applications and their high strength-to-weight ratio makes them valuable in aviation and space technology. With better understanding of Ti phase diagrams, it may be possible to reduce titanium processing costs so that titanium alloys could substitute for some stainless steels, as a means of reducing the U.S. dependence on imported chromium. Increased knowledge of Ti alloy phase formation can provide means of improving weldability.

Experimental work on these Ti-Al systems at NBS has been designed to overcome the experimental difficulties which have resulted in conflicting reports of several Ti diagrams in the literature. Contamination easily occurs in long anneals: principally, oxygen cannot be removed, and the presence of Al may make hydrogen removal difficult as well. Special attention has been given to the production of pure samples: the oxygen content of samples now being prepared is less than 350 ppm, very low for Ti alloys. With carefully prepared samples we have investigated selected regions of the phase boundaries using TEM, optical metallography, and differential scanning calorimetry (DSC). Prof. R. C. Reno, who is visiting NBS from the University of Maryland, has made the TEM measurements for these studies. In addition, the order/disorder transition in the binary Ti-Al system has been studied using magnetic susceptibility measurements.

The phases being investigated are the bcc solid solution (β), the disordered hcp solid solution (α), and the ordered hcp phase (α'). After precision determinations of the β/α and α/α' boundaries had been made in the binary Ti-Al system, the effect of 0.25 a/o Mo on the $\alpha/(\alpha + \beta)$ and $\alpha/\alpha + \alpha'$ was monitored; thus the Ti-Al edge of the ternary Ti-Al-Mo diagram is mapped. The effect of oxygen on these boundaries in the ternary Ti-Al-O system also is being determined. For the first time the order/disorder transition α/α' has been monitored using DSC, and the α/α' transition has been shown to be relevant for the study of the Ti6211 alloy.

Experiments have been done in conjunction with theoretical work on these systems: Cahn and Kikuchi have modeled the order/disorder transition using the cluster-variation method. A determination of the effect of Nb on the phase boundaries to parallel the Ti-Al-Mo work will establish an equivalency relationship between additions of Mo and of Nb, and this is expected to contribute to our understanding of the thermodynamics of the binary Ti-Mo and Ti-Nb systems as well as the ternary systems.

Other experiments of fundamental significance to phase stability are underway. Dr. David Goodman, a postdoctoral research associate, is investigating the thermodynamic properties of Ti-Al alloys using a solid electrolyte electrochemical technique. Metallic glasses and metastable crystalline compounds are another class of material of great interest. They have often been found to possess more desirable properties (e.g., corrosion resistance, strength, hardness, and ductility) than their equilibrium counterparts. In pursuit of this interest, a vacuum melt spinner has been constructed in which the molten alloy is solidified very quickly by impinging the liquid onto a copper wheel rotating at a speed of 10,000 rpm. For a glass produced in a 77 Pd-6 Cu-17 Si alloy, Dr. Moshe Rosen, a visitor to NBS from Johns Hopkins University, has succeeded in monitoring its crystallization by ultrasound velocity measurements.

Fundamental Theory. In collaboration with Dr. R. E. Watson, further advances have been made in the understanding of parameters important to alloy phase stability. Two papers comparing data with predictions of the heat of formation of binary transition metal alloys appeared in CALPHAD. Some of these predicted heats have been used by the Harwell group in their calculations of multicomponent uranium alloy systems.

Literature data on Mössbauer isomer shifts for dilute alloys have been reinterpreted in terms of d-band hybridization, and in terms of solubility limits for terminal solid solutions of transition metal alloys. Goodman, Cahn, and Bennett have published a paper on the thermodynamic restrictions on the slopes of phase boundaries. Work is in progress on a theoretical understanding of the role of charge transfer in transition metal solubility asymmetry.

Our activity in ASTM continues. Task workers participate in ASTM Committees D32 on Catalysis, E42 on Surface Analysis, E13 on Molecular Spectroscopy, B5 on Cu and Cu Alloys, and E7 on Nondestructive Evaluation. L. H. Bennett serves as an officer of the Committee on Alloy Phases of the Metallurgical Society of AIME. L. H. Bennett and J. R. Cuthill are the official NBS representatives on the Joint ASTM-SAE Committee on the Unified Numbering System in Metals and Alloys.

Alloys for Catalysis and Fuel Cells
Subtask 2 of Task 12145

A. J. McAlister

Development of successful fuel cells will increase significantly the efficiency of fuel utilization and markedly reduce our national dependence on foreign energy sources. For low temperatures acid fuel cells, a number of problems are performance limiting. Scarce and expensive Pt, now used as both fuel and air catalysts should be replaced or more efficiently used, and air catalyst supports more resistant to corrosion at cathodic potentials are needed. Despite these difficulties, many practical advances are being made. The Department of Defense (DOD) has successfully employed small cells of a few kilowatt capacity in transportation and portable power source applications, while in the area of power generation, Department of Energy (DOE) and Electric Power Research Institute (EPRI) have sponsored a 4.8 MW, naptha-fed assembly which is soon to be installed in the New York City power net.

Our research involvement in this area has focused principally on CO tolerant H_2 oxidation anode catalysts for use in low temperature acid electrolyte fuel cells. In earlier studies, we were the first to demonstrate activity and voltage stability in Re metal, $W_{1-x}Ti_xC$, WP, and $W_{1-x}Mo_xC$, the latter isostructural with the known strong CO resistant fuel electrocatalyst, WC. Comparative studies of WC and Mo rich $W_{1-x}Mo_xC$ showed these alloys to be equally corrosion resistant, catalytically active for H_2 oxidation, and CO tolerant. In addition, we demonstrated that proton discharge is rate limiting on these carbides, in contrast to Pt where chemisorptive dissociation is the slow step. Anode catalysts of Pt dispersed on WC were studied as well. Pt, like chemically similar Co and Ni, had been predicted to surface segregate on WC, perhaps wetting it as well. Hence, the formation of surface phases was anticipated, and expected to provide not only more efficient use of Pt, but desirable catalytic properties intermediate between those of highly active but CO sensitive Pt and less active but CO resistant WC. Light loadings of Pt on WC (nominal partial monolayers) showed the anticipated behavior. In pure H_2, these preparations were about a tenth as active overall as similar loadings of Pt on carbon supports, but in three percent CO/H_2, over ten times as active as equivalent areas of Pt sheet.

During the past year we have more thoroughly characterized the Pt/WC dispersions via electrochemical characterization techniques, and analyzed their performance by nonlinear least squares fitting of the polarization curves in pure H_2 and CO contaminated fuel feeds. We also have addressed the strong variation of the activity of WC with mode of sample preparation via analysis of our own and literature data, and studied the dependence of the H_2 oxidation activity of $W_{1-x}Ti_xC$ on W concentration and C defect concentration. Taken together, these data yield a viable model of the active sites on transition metal carbides, quantitative understanding of the surface density of active sites, and some preliminary insight into the systematics of CO tolerance on the carbides.

Analysis of the Pt/WC data indicates that all dispersions studied contained a small fraction of crystalline Pt, whose contributions could be eliminated via computer modeling using the known rate constants of Pt. The residual highly dispersed, perhaps atomically dispersed, form of Pt on WC has the following properties: Tafel kinetics with transfer coefficient of 0.5 (vs 0.3 for WC); exchange current density in H_2 approximately four times that of the WC, dropping in three percent CO/H_2 to about the same as that of the host WC.

Studies of $W_{1-x}Ti_xC_{1-y}$ through the range of stability of the bcc phase revealed: no activity for TiC_{1-y}; Tafel kinetics with a transfer coefficient of ~ 0.2 when $1-x > 0$; complete CO tolerance (as in WC); variation in exchange current density proportional to $y(1-x)^2$; and activation energy approximately equal to that of WC.

The carbon defect densities, y, of highly active WC's were estimated from published chemical and Auger analyses; those of our $W_{1-x}Ti_xC_{1-y}$ samples from chemical analysis and phase stability data. A plot of H_2 oxidation activity (corrected for differences in temperature, acid concentration, and in the case of $W_{1-x}Ti_xC$, for W concentration via a factor of $[1-x]^{-2}$) vs y shows a common linear variation. We conclude from these results that the active site on the carbides consists of two or more W (or W and Pt) near neighbors of a carbon defect. Hence the very active WC samples are carbon deficient metastable alloys (WC being nearly a line compound in the equilibrium phase diagram.)

Other data, accumulated over the last several years, in our laboratory and elsewhere, indicate that a strong electronic factor underlies H_2 oxidation activity in transition metals and transition metal-metalloid compounds: for metal atoms in the active complex, the Fermi level must fall in the upper d-band region in which the d-orbitals are of anti-bonding type. CO tolerance occurs when this d-band region is just partially filled; CO poisioning occurs when it is nearly filled. Additionally, our work during the past year suggests that a geometric factor exists as well in the compounds; appropriate H-metal potentials occur only when electronically favorable surface metal atoms relax about a carbon defect. Ultimate H_2 oxidation performance in compound catalysts appears to lie in the selection and production of highly metalloid defective metastable alloys.

A. J. McAlister is a member of ASTM Committees E42 on Surface Analysis and D32 on Catalysis.

Nondestructive Evaluation of Nonuniformities in 2219 Aluminum Alloy Plate-Relationship to Processing
Subtask 3 of Task 12145

L. K. Ives, L. J. Swartzendruber, W. J. Boettinger, M. Rosen, S. D. Ridder, F. S. Biancaniello, R. C. Reno, S. Fick, D. B. Ballard, R. Mehrabian

This task was initiated at the National Bureau of Standards at the request of the National Aeronautics and Space administration shortly after the announcement in August 1979 by the Reynolds Metal Company that about 31 million pounds of aluminum were suspected of containing "soft" spots due to a possible malfunction

in the water cooling system at one manufacturing plant. Some of these "soft" spots were reported to be as much as 45 percent below the strength specifications used for the purchase of the aluminum by aircraft manufacturers and suppliers.

The initial concern of this task was the 2219-T87 aluminum alloy used extensively on the space shuttle. The results of our investigations on this alloy were used by the sponsoring agency to ensure that the testing necessary to prove structural integrity had been accomplished prior to launch. The results also had the fortunate effect of expediting the space shuttle launch by eliminating a large amount of unnecessary testing.

The major portion of the work on the 2219 alloy has been concluded and attention is now being focused on 2024 alloy, an alloy which is more widely used in the construction of commercial aircraft. Our results established that better nondestructive evaluation (NDE) techniques are needed for quickly judging the strength of an aluminum plate throughout its thickness rather than simply on the surface as given by hardness and conductivity. As a result, on-going investigations of the feasibility of using an ultrasonic technique as an alternative are being carried out on both the 2219 and 2024 alloys.

As with the studies on 2219 alloy, the goal of this task is to develop specific relationships between processing variables used during ingot casting, mechanical working, and heat treatment of the 2024 aluminum alloy, and the resulting microstructures, mechanical properties, and NDE responses. This detailed blend of metallurgical examination of the alloy with its NDE response is necessary not only to attack the specific problem at hand but also to gain a fundamental knowledge of the features of metallurgical microstructures which cause changes in NDE parameters. Work in this program is divided into five areas: (1) Studies on as-received plate of 2024 aluminum alloy. This is motivated by the realization that the properties vary across plate thickness. These variations can have different effects on various NDE techniques. (2) Solidification-segregation studies. Part of the variation in properties across finished alloy plate is caused by segregation of the alloy components (Cu, Mn) during ingot casting. (3) Determination of time-temperature transformation diagrams (C-curves) and the relationship between mechanical properties and conductivity. Samples produced during various thermomechanical treatment have a wide range of mechanical properties (hardness, yield strength, tensile strength) and conductivity. (4) Electron microscopy studies done on the wide range of metallurgical microstructures produced. Extremely fine scale ($\sim$ 0.01 μm) particles are responsible for the strength of aluminum alloys and contribute to associated changes in conductivity. (5) Predictions of heat flow conditions during malfunctions of the commerical process (namely slow quenching from the solution heat treatment temperature), and predictions using experimentally determined C-curves of the resultant mechanical property degradations and changes in NDE response.

In the ultransonic studies, continuous monitoring of the sound velocity, ultrasonic attenuation, and hardness during the progress of the aging process in 2219 was corroborated with an examination of the specimens by transmission electron microscopy. The experimental data were interpreted within the framework of established theories of diffusional processes and models of precipitation hardening.

The highlights of this investigation were: (1) Demonstration of the operational feasibility of an ultrasonic NDE method for monitoring the precipitation process in aluminum alloys in real-time, over a wide temperature interval. Figure 1 shows the variation of the sound velocity (elastic moduli) during the aging process. The minima represent the maximum rate of formation of specific precipitates. Figure 2 shows the changes in the sound wave attenuation (absorption of energy) while the samples undergo the precipitation hardening. The peaks are related to the formation of the particles as well as to the loss of coherency (denoted by 3) of the precipitates with the aluminum matrix. (2) Determination of the mechanism and the kinetics of precipitation by simultaneous measurements of changes in sound-wave and attenuation. (3) Calculation of the activation energies and other characteristic parameters related to the formation and growth of precipitates. (4) Elucidation of the relationship between the nature of the precipitates and their specific contribution to strength and hardness of the alloy. In this context the occurrence of attenuation peaks at aging times when hardness peaks are developed, indicating the loss of coherency of the precipitates with the matrix, is noteworthy in figure 2. In addition, the effect of prior plastic deformation and the aging process was considered.

The development of NDE ultrasonic experimental techniques and their use in obtaining the data in this investigation have required research of both a practical and basic nature. The extension of techniques for ultrasonic NDE to industrial applications requiring on-line, real-time monitoring during thermo-mechanical treatment necessitates further development efforts. Improved control of material properties important to the end user offers additional motivation for further study of basic phenomena, e.g., kinetics and mechanism of the aging process in single crystal specimens in order to determine the specific contribution of precipitates on the prominent crystal planes, and the effects of applied uniaxial and hydrostatic stresses during the precipitation process.

The investigation of 2024 aluminum alloy will be completed during FY82 when a final report on this alloy will be issued to the sponsor. The large amount of data and the techniques developed are expected to be of value for improving both the nondestructive evaluation of the finished product and the processing of material.

Other Activities of the Metallurgy Division

Invited Talks

The Use of Metals as Surgical Implants
ASM Central Virginia Chapter, Lynchburg, Virginia
A. C. Fraker
October 3, 1980

Application of Transmission Electron Microscopy to the Study of Wear
ASM Seminar on Wear and Friction, Pittsburgh, Pennsylvania
L. K. Ives
October 5, 1980

Sliding Wear of Steels
ASM Seminar on Wear and Friction, Pittsburgh, Pennsylvania
A. W. Ruff
October 5, 1980

Basic Mechanisms of Atomic Redistribution in Alloys Undergoing Irradiation
1980 TMS-AIME Fall Meeting, Pittsburgh, Pennsylvania
J. R. Manning
October 6, 1980

Direct Correlation Between Microstructure and Acoustic Emission Using Indentation Methods
Metallurgical Society, AIME, Pittsburgh, Pennsylvania
R. B. Clough
October 7, 1980

Relationship Between Process Variables, Microstructure, and NDE of a Precipitation-Hardened Aluminum Alloy
TMS-AIME Fall Meeting, Pittsburgh, Pennsylvania
W. J. Boettinger
October 7, 1980

Nondestructive Evaluation of Nonuniformities in Aluminum Alloy Plate
ASNT Fall Conference, Houston, Texas
L. J. Swartzendruber
October 7, 1980

Wear Mitigation in Valves for Coal Conversion Systems
Second Symposium on Valves for Coal Conversion and Utilization, Morgantown, West Virginia
K. J. Bhansali
October 16, 1980

Native Americans in Science
Twelfth Annual Convention of the National Indian Education Association, Dallas, Texas
G. J. Mattamal
October 20, 1980

Uses of Metals as Surgical Implants
Damascus High School, Damascus, Maryland
A. C. VanOrden
October 21, 1980

Corrosion and Fatigue of Surgical Implant Metals
Materials Degradation Lecture Series, Flint, Michigan
A. C. Fraker
October 22, 1980

NBS/NRL Synchrotron Radiation Materials Science Topography Line
Brookhaven NSLS
M. Kuriyama
October, 1980

Overview of Recent Research in Aluminum Alloys
The Aluminum Association, Washington, DC
R. Mehrabian
October 22, 1980

The Use of Metals as Surgical Implants
Joint NACE/ASM Meeting, Richmond, Virginia
A. C. Fraker
November 11, 1980

Role of Metallurgical Structure in the Integrity of Sliding Solid Contacts
ASME Symposium of Solid Contact and Lubrication, Chicago, Illinois
P. J. Blau
November 18, 1980

Nuclear Resonance and Its Application to Alloys
Materials Research Society, Boston, Massachusetts
L. H. Bennett
November 19, 1980

Research at NBS in Metals For Use in Bioimplants
University of Maryland, College Park, Maryland
A. C. VanOrden
December 1, 1980

Abrasive Wear Resistance Considerations in Metallurgical Coatings
NASA Lewis Center, Cleveland, Ohio
K. J. Bhansali
December 4, 1980

Surface Flows and Surface Tensions for Liquid Gallium
Float Zone Processing Meeting, Huntsville, Alabama
J. R. Manning
December 12, 1980

Theory of Acoustic Emission
Metals Society and Institute of Physics, Oxford University, Oxford, England
J. A. Simmons
December 17, 1980

The Use of Metals as Surgical Implants
ASM West Virginia Chapter, Charleston, West Virginia
A. C. Fraker
January 20, 1981

EXAFS Spectroscopy in Material Science
College of William & Mary, Physics Dept.
G. Cohen
February 6, 1981

Corrosion and Fatigue of Implant Metals
Johns Hopkins University, Baltimore, Maryland
A. C. Fraker
February 24, 1981

Research on Metals for Bioimplants at NBS
Langley High School, Langley, Virginia
A. C. VanOrden
March 20, 1981

Scientific Research Activities and Opportunities at NBS
Clarkson College, Potsdam, New York
G. J. Mattamal
March 25, 1981

Uses of Metals as Surgical Implants
Gaithersburg Junior High School, Gaithersburg, Maryland
A. C. VanOrden
March 27, 1981

Observations on the Wear-In Process During the Sliding of Several Copper Alloys Against 52100 Steel
ASME Wear of Materials Conference, San Francisco, California
P. J. Blau
March 30, 1981

Sliding Wear Behavior of Electron Beam Surface Melted O-2 Tool Steel
ASME Wear of Materials Conference, San Francisco, California
A. W. Ruff
March 31, 1981

Role of Stacking Fault Energy on the Galling and Wear Behavior of a Cobalt Base Alloy
ASME Wear of Materials Conference, San Francisco, California
K. J. Bhansali
March 31, 1981

Microscopic Aspects of Wear of Metals
Naval Air Development Center, Warminster, Pennsylvania
A. W. Ruff
April 15, 1981

X-ray Absorption Spectroscopy of Metallic Material
University of Maryland, Physics Dept.
G. Cohen
April 27, 1981

Wear Studies on Surface Melted Alloys
University of Minnesota, Minneapolis, Minnesota
A. W. Ruff
May 5, 1981

The Influence of Heat Treatment on the Fatigue Life of Ti-6Al-4V and Ti-4.5Al-5Mo-1.5Cr
ASTM Symposium - Titanium and Its Alloys for Surgical Implants, Phoenix Arizona
A. C. Fraker
May 12, 1981

Surface Preparation and Corrosion Behavior of Titanium Alloys for Surgical Implants
ASTM Symposium--Titanium and Its Alloys for Surgical Implants, Phoenix, Arizona
A. C. Fraker
May 12, 1981

Uses of Metals as Surgical Implants
North Bethesda Junior High School, Bethesda, Maryland
A. C. VanOrden
May 15, 1981

Indentation Acoustic Emission--A New Method for Correlating AE Signals with Microstructure
Fourth International Conference on NDE in the Nuclear Industry, Lindau, West Germany
R. B. Clough
May 25, 1981

Science-Career Opportunities for Both Graduate and Undergraduate Students at NBS
University of Minnesota, Minneapolis, Minnesota
G. J. Mattamal
May 29, 1981

Acoustic Emission Source Characterization in Plate Material
IZfP, Saarbrucken, West Germany
R. B. Clough
June 1, 1981

Applications of a High Intensity Laboratory X-ray Source to EXAFS Spectroscopy
University of Michigan, Physics Dept., Ann Arbor, Michigan
G. Cohen
June 10, 1981

Synchrotron Radiation Topography Lines at NSLS
DOT, Cambridge, Massachusetts
M. Kuriyama
June 16, 1981

RST Methods and Generic Programs
COMAT/RST Briefing/Workshop, NBS, Gaithersburg, Maryland
R. Mehrabian
July 1, 1981

Fundamentals of Rapid Solidification
Materials Research Council Meeting, La Jolla, California
R. Mehrabian
July 7, 1981

Observations on Wear
Gordon Research Conference on Physical Metallurgy, Andover, New Hampshire
A. W. Ruff
July 9, 1981

Physics of Alloys and Alloy Phase Diagrams
Brandeis University, Waltham, Massachusetts
L. H. Bennett
July 13, 1981

Synchrotron Radiation Topography Lines at NSLS
Denver, Colorado
M. Kuriyama
August 5, 1981

Use of Synchrotron Radiation for Materials Science at NBS
Tokyo University, Tokyo, Japan
W. J. Boettinger
August 10, 1981

Use of Synchrotron Radiation for Materials Science at NBS
National Laboratory for High Energy Physics (Photon Factory), Tsukuba, Japan
W. J. Boettinger
August 11, 1981

The Effect of Alloy Constitution and Crystallization Kinetics on the Formation of Metallic Glass
Department of Engineering Science, Kyoto University, Kyoto, Japan
W. J. Boettinger
August 14, 1981

The Effect of Alloy Constitution and Crystallization Kinetics on the Formation of Metallic Glass
Department of Metallurgy, Nagoya University, Nagoya, Japan
W. J. Boettinger
August 18, 1981

The Effect of Alloy Constitution and Crystallization Kinetics on the Formation of Metallic Glass
Fourth International Conference on Rapidly Quenched Metals, Sendai, Japan
W. J. Boettinger
August 25, 1981

Technical and Professional Committee Participation and Leadership

American Association for Crystal Growth
S. R. Coriell and R. L. Parker, Executive Committee

American Chemical Society
G. J. Mattamal, Member

American Foundrymen's Society
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Solidification Committee of the Metallurgical Society
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P. J. Blau, Executive Committee, Washington Chapter
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A. W. Ruff, Program Committee, Washington Chapter
C. J. Bechtoldt and R. Mehrabian, Members, Washington Chapter

Bulletin of Alloy Phase Diagrams
L. H. Bennett, Editor
D. J. Kahan and M. E. Read, Associate Editors
R. V. Drew, Assistant to the Editor

Mass Transport Activity
J. R. Manning, Member

Phase Transformations Committee
R. Mehrabian, Member

Process Modeling Activity
J. R. Manning and R. Mehrabian, Members

American Society for Metals/American Institute of Metallurgical Engineers
Composite Committee
R. Mehrabian, Member

International Council for the ASM/NBS Program for Alloy Phase Diagrams
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Handbook Committee on Definitions
J. R. Cuthill, Member

American Society of Mechanical Engineers
Research Committee on Lubrication (Hardfacing and Coatings)
K. J. Bhansali, Member

American Society of Mechanical Engineers/American Society for Metals
Wear of Materials Conference Steering Committee
A. W. Ruff, Member

American Society for Testing and Materials
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R. L. Parker, Member

B2: Nonferrous Metals and Alloys
S. D. Ridder, Member

B5: Copper and Copper Alloys
M. E. Read and L. J. Swartzendruber, Members

B6: Die-Cast Metals and Alloys
R. Mehrabian, Chairman

B7: Light Metals and Alloys; Aluminum Alloy Ingots and Castings
W. J. Boettinger and R. D. Shull, Members

B9: Metal Powders and Metal Powder Products
J. R. Manning, Member

D32: Catalysts
A. J. McAlister, Member

E4: Metallography
D. B. Ballard, P. J. Blau and L. J. Swartzendruber, Members

Task Group on Microhardness Testing
P. J. Blau, Member

E4.11.07: Metallography; Electron Metallography; Scanning Electron Microscopy
D. B. Ballard, Task Group Leader

E42: Surface Analysis
J. R. Cuthill, Past Chairman
G. G. Cohen, A. J. McAlister, Members

E7: Nondestructive Testing
L. H. Bennett and L. J. Swartzendruber, Members

E7.04 Acoustic Emission
J. A. Simmons and R. B. Clough, Members

Joint Task Group on Acoustic Emission; Sensitivity Calibration
J. A. Simmons, Chairman

F4: Medical and Surgical Materials and Devices
A. C. Fraker and A. W. Ruff, Members

F4/G1: Joint Section on Corrosion of Implants
A. C. Fraker, Co-Chairperson

G2: Erosion and Wear
A. W. Ruff, Vice Chairman

G2.2 Solid Particle Erosion
A. W. Ruff, Task Group Leader
K. J. Bhansali, Member

G2.91: Terminology and Definitions
L. K. Ives, Chairman
P. J. Blau, Vice Chairman

American Vacuum Society
D. B. Ballard, Member

Applied Mechanics Reviews
R. B. Clough, Member, Review Staff

Florence Review Committee, Review of Scanning Electron Microscopes
D. B. Ballard, Chairman

International Association for Dental Research
G. J. Mattamal, Member

International Journal of Crystal Growth
R. L. Parker, Deputy Principal Editor, Editorial Board

International Organization of Crystal Growth
R. L. Parker, Council Member

International Journal of Diffusion and Defect Data
D. B. Butrymowicz, Advisory Board Member

International Council of Science Unions, Committee on Space Research (COSPAR)
R. L. Parker, Member

Maryland Institute of Metals
W. J. Boettinger, Executive Board Member

Materials Processing Center, Massachusetts Institute of Technology
R. Mehrabian, Member Advisory Board

Materials Science and Engineering
L. H. Bennett, Editor, Phase Diagram Section

Metallography, Journal of International Metallographic Society
J. R. Cuthill, Member, Editorial Advisory Board

Metallurgical Transactions
L. H. Bennett and R. Mehrabian, Members, Board of Review

Visiting Committee, Department of Metallurgy and Materials Science Carnegie-Mellon University
R. Mehrabian and R. L. Parker, Members

National Aeronautics and Space Administration, Space and Terrestrial Applications Steering Committee, Proposal Evaluation Advisory Subcommittee
S. R. Coriell, Member

National Aeronautics and Space Administration, Universities Space Research Association
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National Materials Advisory Board, Committee on Aluminum Powder Alloys
J. R. Manning, Member

National Materials Advisory Board, Committee on Superalloy Powder Alloys
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National Materials Advisory Board, Committee on Amorphous and Metastable Materials
R. Mehrabian, Member

National Materials Advisory Board, Committee on Materials Substitution Methodology
R. Mehrabian, Liaison Member

National Science Foundation, Facilities Subcommittee of the Materials Research Advisory Committee
G. G. Cohen, Chairman

Rapid Solidification Technology Briefing/Workshop, 1981
R. Mehrabian, Chairman
J. R. Manning, Member, Organizing Committee

Society of Automotive Engineers/American Society of Testing and Materials Unified Numbering System for Metals and Alloys
L. H. Bennett, NBS Representative
J. R. Cuthill, Alternate Representative

Society for Biomaterials Standards Committee
A. C. Fraker, Chairperson

Society for Experimental Stress Analysis, Residual Stress Committee
C. J. Bechtoldt, Member

Society of Rheology
R. Mehrabian, Member

US-USSR Technology Exchange Agreement, Sub-committee on Electro-Slag Remelting
R. Mehrabian, Member

Welding Research Council, Committee on Hardfacing and Wear
K. J. Bhansali, Member

External Recognition

Fellow, American Society for Metals
October 1980
J. R. Cuthill

Fellow, American Society for Testing and Materials
October 1980
J. R. Cuthill

George Kimball Burgess Memorial Award
American Society for Metals, Washington DC Chapter
May 1981
J. R. Cuthill

Books

Critical Issues in Materials and Mechanical Engineering
Edited by J. T. Fong, R. C. Dobbyn and L. Mordfin
ASME, PVP-Vol. 47, New York, 1981

Wear of Materials, 1981
Edited by S. K. Rhee, K. C. Ludema, and A. W. Ruff
American Society for Mechanical Engineers

Special Reports

NBS: NDE of Nonuniformities in 2219 Aluminum Alloy Plate--Relation to Processing
L. J. Swartzendruber, W. J. Boettinger, L. K. Ives, S. R. Coriell, D. B. Ballard, D. E. Laughlin, R. B. Clough, F. S. Biancaniello, P. J. Blau, J. W. Cahn, R. Mehrabian, G. Free, H. Berger, and L. Mordfin
NBSIR 80-2069

NBS: Materials Measurement
J. R. Manning
NBSIR 81-2295

Sponsored Conferences

Rapid Solidification Technology Briefing/Workshop
NBS, Gaithersburg, Maryland
July 1-2, 1981
R. Mehrabian, Chairman
J. R. Manning, Member, Organizing Committee

International Conference on Wear of Materials
San Francisco, California
March 30 - April 2, 1981
A. W. Ruff, Program Chairman

Innovation for Maintenance Technology Improvements
Mechanical Failures Prevention Group
NBS, Gaithersburg, Maryland
April 21-23, 1981
A. W. Ruff, Organizing Committee Chairman

Materials Evaluation Under Fretting Conditions
ASTM/NBS Joint Symposium
NBS, Gaithersburg, Maryland
June 3, 1981
A. W. Ruff, Organizing Committee Member

Publications

Characterization of Wear Surfaces and Wear Debris
A. W. Ruff, L. K. Ives, and W. A. Glaeser
Fundamentals of Friction and Wear
American Society for Metals (1980)

Crystals and Focusing Arrangements for Laboratory EXAFS
G. G. Cohen and R. D. Deslattes
Proc. of a Workshop on Laboratory EXAFS (1980)

Quantitative Kinetic and Morphological Studies Using Model Systems
R. J. Schaefer and M. E. Glicksman
Proc. of Conf. on Modeling of Casting and Welding Processes (1980)

A Review of Our Present Understanding of Macrosegregation in Axi-Symmetric Ingots
S. D. Ridder, R. Mehrabian, and S. Kou
Proc. of Conf. on Modeling, Casting, and Welding Processing (1980)

Nondestructive Evaluation of Nonuniformities in Aluminum Alloy Plate
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ASTM Special Technical Publication (to be published)

Division Seminars

Abrasive Wear of Materials
O. Vingsbo
Uppsala University, Sweden
October 2, 1980

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A. V. Levy
University of California, Berkeley, California
October 8, 1980

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N. J. Petch
University of Strathclyde, Glasgow, United Kingdom
October 16, 1980

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T. B. Massalski
Carnegie-Mellon University, Pittsburgh, Pennslyvania
December 2, 1980

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W. J. Boettinger
National Bureau of Standards, Washington, DC
December 9, 1980

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L. Swartzendruber
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L. K. Ives
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Text Editing Facilities at NML
E. Ring
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W. C. Johnson
National Bureau of Standards, Washington, DC
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G. J. Abbaschian
University of Florida, Gainesville, Florida
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D. P. Pope
University of Pennsylvania, Philadelphia, Pennsylvania
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S. Ramalingam
Georgia Institute of Technology, Atlanta, Georgia
February 9, 1981

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P. J. Blau
National Bureau of Standards, Washington, DC
February 17, 1981

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C. J. Bechtoldt
National Bureau of Standards, Washington, DC
March 3, 1981

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J. Kameda
University of Pennslyvania, Philadelphia, Pennsylvania
March 13, 1981

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A. E. Miller
University of Notre Dame, Notre Dame, Indiana
March 17, 1981

Laser Generated Ultrasound in Metals
D. Hutchins
Technical University of Nova Scotia, Halifax, Nova Scotia, Canada
March 24, 1981

Wear in Polymer Micropairs
Z. Rymuza
Warsaw Technical University, Warsaw, Poland
March 26, 1981

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R. Dressler
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A. Hellawell
Michigan Technological University, Houghton, Michigan
April 9, 1981

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K. C. Ludema
University of Michigan, Ann Arbor, Michigan
April 22, 1981

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E. H. Eberhardt
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April 24, 1981

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C. N. Adams
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J. Clark
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R. B. Waterhouse
University of Nottingham, Nottingham, England
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H. I. Aaronson
Carnegie-Mellon University, Pittsburgh, Pennsylvania
June 23, 1981

X-ray Topography of Crystal Growth Defects of Microhardness Indentations, and of Polysilicon Photovoltaic Cells
R. W. Armstrong
University of Maryland, College Park, Maryland
June 30, 1981

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J. H. Perepezko
University of Wisconsin, Madison, Wisconsin
July 7, 1981

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S. H. Carpenter
University of Denver, Denver, Colorado
July 14, 1981

Sliding Wear and Deformation Studies on Experimental Martensitic Steels
W. J. Salesky
University of California, Berkeley, California
July 22, 1981

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H. A. Lipsitt
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July 28, 1981

New Approaches to Crystal Growth From the Melt
A. F. Witt
Massachusetts Institute of Technology, Cambridge, Massachusetts
August 12, 1981

CERAMICS, GLASS, AND SOLID STATE SCIENCE DIVISION

CERAMICS, GLASS, AND SOLID STATE SCIENCE DIVISION (565)

Thomas D. Coyle, Chief (Acting)
Samuel J. Schneider, Deputy Chief (Acting)
B. A. Hyde, Secretary
M. A. Clevinger, Secretary
E. R. Smith, Secretary
M. M. Barbosa, Secretary

The Ceramics, Glass, and Solid State Science Division provides measurement services, concepts, and critical data needed for improved utilization of several categories of technologically important materials: ceramics, glass, and optical materials. The program of the Division involves the integration of several disciplines: solid state chemistry, crystallography, and solid state physics devoted to the characterization and the understanding of the behavior of these materials throughout their life cycle. Emphasis is on the details of microstructure and on high temperature/high pressure effects. The nature of the work is both fundamental and applied with major outputs focused on new measurement techniques, reference and engineering data, and standard reference materials.

The Division's research activities are supportive of and intimately connected to the needs of industry and other Government organizations. Our Research Associate Program with the JCPDS-International Centre for Diffraction Data, for instance, provides x-ray powder data, standards, and compilations used the world over for materials characterization. Coupled with this is our experimental effort to improve x-ray techniques for quantitative phase analysis; a factor of five improvement over state-of-the-art has been achieved. Similarly, the "Phase Diagrams for Ceramists" data compilation series, prepared jointly with the American Ceramic Society, is a major set of reference texts used extensively by the ceramics, glass, and metals communities. Companion experimental phase equilibria work currently centers on systems primarily important to refractory corrosion control in the steel and energy technologies. An important adjunct to the phase equilibria studies is the recent development of a fluidic temperature sensor having increased durability in corrosive, high temperature environments. In the glass area, we have recently produced a liquidus temperature SRM, an assortment of glass standards for chemical (instrumental) analysis, and currently we are working toward nuclear waste leachability (glass) standards.

Our work with other Government organizations is also extensive; it includes cooperative programs with the Department of Energy (flyash characterization, nuclear waste form research, coal slag chemistry, laser glasses, thin films, fossil energy materials data center); Harry Diamond Laboratories (fluidic sensors); Office of Naval Research (optical properties); Oak Ridge National Laboratory (structural ceramics); and Watervliet Arsenal (high pressures).

The Division's accomplishments during FY81 are described in the following pages in terms of three tasks:

12151	STRUCTURAL CHEMISTRY FOR CERAMIC PROCESSING AND DURABILITY
12153	STRUCTURAL METHODS FOR PROCESSING, MANUFACTURING, AND DURABILITY
12154	GLASS AND OPTICAL PROPERTIES

STRUCTURAL CHEMISTRY FOR CERAMIC PROCESSING AND DURABILITTY
Task 12151

The major objectives of this task are: to provide methods and obtain data for the construction, compilation, and evaluation of phase diagrams of systems containing oxides, sulfides, oxynitrides, etc. Attention is focused on silicates with additions of one to six other oxides, which form the basis of the very important (coal) slags; to study the composition, phases, and properties of various oxide systems with either random or ordered defects or incommensurate (modulated) structures and to interpret the relation between the charge transport mechanisms and nonstoichiometry of these compounds; and to assess the potential of ceramics and related materials for use in energy conversion devices, for catalyzing chemical processes, and for storing both beneficial and harmful elements and compounds.

As these objectives are very broad it is necessary to be more specific in the subtasks under investigation. The materials actually examined in the course of this study can be divided into two groups. The first group consists of the seven most abundant oxides in the earth's crust which make up the composition of coal slag and of most high volume refractory ceramic materials (Na_2O, K_2O, CaO, MgO, FeO_x, Al_2O_3, SiO_2). The second group consists of materials of interest in high technology ceramics, for electronics, electrodes, catalysts, ionic conductors, dielectrics, etc.

The experimental determination of complex phase equilibria in a multicomponent system is a very laborious and time-consuming effort. Therefore, we are seriously examining existing computer programs for prediction of phase equilibria from thermochemical data. We hope eventually to be able to modify such programs to be useful for the prediction of solid-solid and solid-liquid equilibria in complex systems of interest to the ceramic industry.

During the last several years and especially since July 1974, as a response to the national need, much of the work has been directed to the area of materials research for energy conversion. Most staff members in the task are now working directly on materials problems in several energy-related disciplines, for example, ceramics for MHD, gas turbines, batteries, and fuel cells. At the request of DOE and DOD, members of the task have begun several new projects, one on ceramics for temperature measurement utilizing fluidic circuitry in extreme environments, and another program on the possible use of ceramics as hosts for nuclear waste storage.

Phase Diagrams for Ceramists
Subtask 1 of Task 12151

L. P. Cook, R. S. Roth, T. Negas

Progress has been made in several areas during the fiscal year. It is anticipated that the major accomplishment for this fiscal year will be the publication of Volume 4, "Phase Diagrams for Ceramists." This volume, the first published since 1975, contains 591 new diagrams with commentaries prepared by more than 15 experts in the field of phase equilibria. The series is under the general editorship of NBS staff, who also assist with the evaluations, and are responsible for maintaining the "Phase Diagrams for Ceramists" data base,

a collection of nearly 10,000 references dealing with phase equilibria in ceramic systems. Coverage of systems in Volume 4 can be broken down as follows: metals and oxygen-112; oxides-394; carbonates-29; chlorates, nitrates, etc.-11; sulfates-15; mixed radicals-29. The author and chemical indices for Volume 4 were prepared at NBS from magnetic tape files set up on an intelligent terminal which were then transferred to the NBS central computing facility, sorted, and edited. The final result was copied on magnetic tape and sent to the American Ceramic Society for use with their computerized typesetting system. Once the problems associated with compatibility of the two computer systems are solved, this method should ease the workload associated with preparation of indices.

It is expected that final editing of Volume 5 will be well under way by the end of FY81. This volume will contain 751 diagrams, broken down as follows: bromides-42; chlorides-107; fluorides-91; iodides-39; mixed halides-60; halides with elements-35; halides with oxides-98; halides with oxygen-containing radicals-32; sulfides-29; sulfides with other substances-49; oxycarbides and oxynitrides-14; aqueous systems-122; systems with other inorganic volatiles-33.

New categories added since the 1975 Supplement includes the sialons, a technologically important family of materials whose application is rapidly expanding. Systems of nitrides and carbides without oxygen, however, are not at present included in the compilation, nor are borides, since these refractory substances are considered by many to be alloys and are covered in separate compilations. Similarly, systems of semiconductors only (silicides, phosphides, arsenides, antimonides, selenides, tellurides) are not included, as these resemble metallic systems more closely. Volume 5 will also contain the cumulative author and chemical indices for the entire five volumes of the series. Preparation of these indices would not have been feasible without the use of the central computing facility and an intelligent terminal. (For example, the chemical index alone contains in excess of 15,000 lines.) Once final editing of the indices is complete a tape will be sent to the American Ceramic Society. Final editing of the commentaries for Volume 5 marks a departure from past practice in that commentaries will be entered on magnetic tape via NBS word processing equipment in a form ready for typesetting, then transferred to the American Ceramic Society. In this way the time required for proofreading should be greatly reduced.

Simultaneously with the completion of Volumes 4 and 5, plans for future supplements continued. At the annual meeting of the American Ceramic Society in Washington, D.C., in May 1981, a luncheon meeting of contributing editors was held to discuss plans and progress. Present at this meeting were: J. J. Brown (Virginia Polytechnic Institute, responsible for fluoride-containing systems), L. L. Y. Chang (University of Maryland, tungstates, molybdates, carbonates, sulfides), F. P. Glasser (University of Aberdeen, alkali oxide containing systems), F. A. Hummel (Pennsylvania State University, formerly responsible for sulfides, phosphates), A. Maun (Pennsylvania State University, transition metal oxides), C. A. Sorrell (University of Missouri-Rolla, aqueous salt systems), K. H. Stern (NRL, binary halides), T. Y. Tien (University of Michigan, oxynitrides), D. R. Wilder and M. F. Berard (Iowa State University, rare earth oxides). The following contributing editors who have recently agreed to participate also attended: E. Kreidler (Ohio State University, tungstates, molybdates), B. Mysen (Geophysical Laboratory, geological systems), T. Rockett

(University of Rhode Island, aqueous cementation systems), J. Weiss (Max Planck Institute, complex multicomponent oxide and oxynitride systems). The following contributing editors were unable to attend: J. P. Coutures (C.N.R.S., rare earth oxides), R. DeVries (General Electric, high pressure work), D. Kolar (Josef Stefan Institute, eastern European studies [R. S. Roth visited Yugoslavia in July 1981]), C. Semler (Ohio State University, refractory oxide systems), R. E. Thoma (Oak Ridge National Laboratory, formerly responsible for molten salt systems). It seems to be the consensus that an accelerated publication schedule is desirable, that increased funding is necessary, and that goals for up-grading the project are reasonable, given increased funding. (As pointed out by several at the luncheon, it is difficult to expect experts to continue to devote time to evaluating phase equilibria on a voluntary basis when their talent can bring in lucrative consulting salaries.)

A poster session describing the on-going "Phase Diagrams for Ceramists" project was also presented at the Annual Meeting of the American Ceramic Society. Considerable interest in the project was expressed by the attendees, and useful feedback was gathered, as well as the opportunity to answer a number of informational requests. As part of the poster session, results of a statistical analysis of material currently being processed for volumes 6/7 were presented. Frequency distributions of references according to country in which the work was done and type of system were discussed. This analysis reaffirmed the large volume of Russian work and the extensive geographical phase equilibrium range of work in the rest of the world. This work is published in many languages and points up the need for continued development of an international system of contributing editors to assist with evaluations. Also there is a growing body of phase equilibrium data for aqueous salt systems, of potential importance for ceramic processing science and studies of ceramic corrosion and durability.

A comprehensive long-range proposal for up-grading the "Phase Diagrams for Ceramists" project in collaboration with the American Ceramic Society was developed during the spring of 1981 and submitted through the Publications Committee to the President of the Society for action at the May Annual Meeting. The proposal assessed current and future needs, set desirable future goals, and devised a plan of action. A three-pronged approach was suggested which involves: (1) provision of adequate support to contributing editors; (2) full utilization of computerized data base management methods, and (3) improved focus of coordinative efforts. These changes will be achieved in large part, it is hoped, by contributions to the American Ceramic Society from the industrial user community, with supplementary funding requested through Government agencies and programs such as the Office of Standard Reference Data. Implementation of the proposed six-year program will result in: (1) publication of supplements to the "Phase Diagrams for Ceramists" series within two years of the current literature at two- to three-year intervals; (2) publication of several soft-bound topical compilations within one year of the current literature, with frequency and coverage according to user demand; (3) publication of semi-annual up-dates of bibliographic phase equilibrium lists, according to chemical system; (4) development of interactive software for storage, retrieval, editing, and plotting of complex ceramic phase equilibrium diagrams; and (5) development of an on-line ceramic phase equilibrium data base service.

A detailed schedule and budget were developed as part of the proposal. To achieve the above goals, ten separate levels of computerization have been outlined:

1. Entry and sort of author bibliography.
2. Entry and sort of chemical bibliography.
3. Development of chemical sequencing programs (complex PDFC format).
4. File management system for processing of new references.
5. Development of "Expanded Bibliographic File."
6. Development of "Commentary File."
7. Development of Advanced Ceramic Phase Diagram Manipulation and Editing Software.
8. Development of "Phase Diagram File."
9. On-line ceramic phase diagram service.
10. Remote editing facilities for contributing editors.

Levels 1 and 2 are essentially complete and considerable progress has been made on levels 3, 4, and 5. A new high speed intelligent terminal with graphics capability has recently been installed, which should aid considerably in increased computerization.

It is hoped that necessary funding will materialize so that Volumes 6/7 of the series can be published according to the accelerated schedule in 1984. The goal is to make these volumes as complete as possible so that all references up through 1981 have been included, and that no references have been overlooked. Evaluations have been prepared for many of the more than 500 references of the first list mailed to contributors for evaluation for Volumes 6/7. A second list with more than 500 new references has been assembled and this material should be mailed to contributing editors by the end of the fiscal year. Two additional lists are planned for late fall and early spring of FY82. Thus, Volumes 6/7 will probably be substantially larger than Volumes 4/5.

Ceramic Ion Conductors
Subtask 2 of Task 12151

R. S. Roth, L. C. Martel

Interest in Li_2O containing phases has been greatly stimulated by the possibilities of Li^+ ion conduction in such phases for use as a solid electrolyte in lightweight, high energy battery systems. The phase equilibria and crystal chemistry of systems combining Li_2O and tetravalent and/or pentavalent metal oxides is largely unknown. The crystal chemistry of the Li_2O-Ta_2O_5 system has been extensively investigated in this laboratory (figure 1). Studies of crystal growth and phase equilibria in this system have been extended to other binary systems of Li_2O with TiO_2, SnO_2, ZrO_2, and ThO_2, and to ternary combinations with Ta_2O_5. The crystal structures of some of the phases and solid solutions encountered have been studied by neutron diffraction total profile analyses in collaboration with Dr. A. Santoro of the Reactor Division and several guest workers, supplemented by single crystal x-ray and neutron diffraction.

In the system Li_2O-ZrO_2 (figure 2) the compound Li_2ZrO_3 was found to form a non-stoichiometric solid solution corresponding to the composition $Li_{2x}ZrO_{3x/2}$ with $x \simeq 0.24$ at $\sim$ 1600 °C. Attempts to introduce defects into the other Li_2MO_3 type phases have been largely unsuccessful. As Li_2SnO_3 has an ordered structure with only Li^+ ions in alternate planes which are connected through Li-Sn planes, the introduction of about ten percent vacancies in the Li^+ concentration would greatly increase the possibilities for ionic conductivity. Unfortunately, the compositions on the join Li_2SnO_3-$LiTaO_3$ do not form a series of solid solutions. The equilibrium relations are broken by a binary join from SnO_2 to the compound Li_3TaO_4, and no appreciable Ta^{+5} is found to substitute for Sn^{+2} in Li_2SnO_3. The same is apparently true for Li_2ZrO_3 (figure 3) although Li_2TiO_3-$LiTaO_3$ may be a true binary join. No compound was found in the system Li_2O-ThO_2, although several new phases have been found in ternary and quaternary combinations in the Li_2O-ThO_2-Ta_2O_5-MoO_3 system.

The crystal structures of Li_2SnO_3 and Li_2ZrO_3 were refined by neutron diffraction total profile analyses in collaboration with J. L. Hodeau, a guest worker from the University of Grenoble, France. One of the surprising results of this study is the observation that the apparent radius of the Li^+ ion is larger than that of either Sn^{+4} or Zr^{+4}. For alkali ion conduction Li^+ is generally considered to be a very small ion which should occur off-center in a tunnel or channel structure. Indeed, the apparently large ionic radius observed may be due to average displacement of Li^+ ions in the channel in three or six directions (depending on the crystallographic symmetry). Unfortunately, the present technique does not have high enough resolution to distinguish between these alternative hypotheses.

The compound Li_3TaO_4 was found to have a quenchable phase transition between 1400° and 1450 °C. The low temperature form was previously described as pseudotetragonal, having an ordered rocksalt-type structure (a') with $a \simeq 12$ a' and $c \simeq 4a'$. The high temperature form was also found to be pseudotetragonal but with $c \simeq 6a'$. Small single crystals can easily be grown in sealed Pt tubes. Single crystal precession patterns reveal that the true unit cell is C-centered monoclinic with $a(\simeq 12a') = 6.024$, $b = 6.006$, $c = 13.326$A, $\beta = 103°3'$. All crystals of the low temperature form, grown between 1200° and 1400 °C, are twinned. A DTA pattern has shown a very small thermal effect around 900 °C. However, it is unlikely that any unquenchable phase transition at this temperature would be a disordered tetragonal structure. A study by the neutron diffraction total profile technique in collaboration with Dr. M. Zocchi of University of Milan, Italy, has revealed that this phase is also really C-centered monoclinic. It is unlikely that the Ta^{+5} ions are mobile enough at 900 °C to disorder and still reorder during quenching. The small DTA peak is probably explainable by some type of disorder and/or mobility of the Li^+ and/or oxygen ions only. The crystal structure of the high temperature form is currently being investigated by both single crystal x-ray and powder neutron diffraction by Dr. Zocchi.

Some studies have also been initiated on the high Li_2O containing phases Li_8SnO_6, Li_7TaO_6, etc. Single crystals of Li_8SnO_6 have been synthesized for the first time, utilizing a common ion flux of only Li_2SnO_3 and Li_2CO_3. These crystals reveal that the rhombohedral symmetry exhibited by the powder pattern is violated by weak, rather diffuse reflections of $h - k + \ell \neq 3n$. This phase will be analyzed by single crystal and powder neutron diffraction to determine the Li^+ crystal chemistry. The possibility of Li^+ defects in Li_8SnO_6 and Li_7TaO_6 are currently being evaluated. A new cubic phase with an ordered rocksalt-like structure (bcc, a = 14.45A) has been synthesized in the system Li_2O-ThO_2-Ta_2O_5-MoO_3 and its composition and stoichiometry are currently being evaluated.

In addition, collaborative studies with Dr. R. J. Cava of Bell Telephone Laboratories are being conducted by neutron diffraction total profile analyses on various Li^+ intercalated phases, $LiReO_3$, Li_2ReO_3 and several vanadates and iron vanadates. The structures of Li_xReO_3 and of $Li_2FeV_3O_8$ were discussed by Dr. Cava at the Gatlinburg Conference on Fast Ion Transport in Solids in May 1981. Single crystals of AgI and CuI were grown by a solution technique for ionic conductivity studies in collaboration with Dr. Cava and a crystal structure analysis was conducted jointly on an iron-niobium selenide prepared by Dr. Cava and Bell Telephone Laboratories.

Nuclear Waste Management
Subtask 3 of Task 12151

R. S. Roth, M. Koob, M. Austin (H. S. Parker)

During this fiscal year R. S. Roth attended a workshop in Seattle, Washington, sponsored by the Materials Characterization Center of Battelle Northwest Laboratories concerning Compositional and Microstructural Analysis of Nuclear Waste Materials and gave an invited lecture on "Phase and Microstructure Analysis" as well as contributed to the workshop on this subject. Another trip was taken to visit the Savannah River Laboratory of DuPont to discuss chemical problems associated with development of a possible "crystalline alternative to glass" for nuclear waste encapsulation. Two papers were presented at the 12th Congress of the International Union of Crystallography concerning some of the BaO-containing phases examined in the present work.

During the current year an effort was made to begin to understand the structural stability of crystalline materials containing large cations, such as Cs^+ in hollandite. This work was necessary as there are few, if any, available data concerning the thermal and structural stability of hollandite minerals containing Ba^+ ions and/or Cs^+ ions in the channels of the Ti-hollandite network. This crystalline phase is the most important of the Cs-containing crystalline constituents of "Synrock" which is under current investigation as a possible host for nuclear waste.

As part of the general studies, the compatibility relations were re-examined for the system BaO-Al_2O_3-TiO_2. The subsolidus relations in this system had been previously reported by Guha. The primary phase fields were roughly

mapped so that small single crystals could be obtained of all the phases. The diagram shown as figure 4 should be considered as very tentative. It has been drawn to be consistent with all the experimental data obtained in the present study, but many more experiments would be needed to more accurately locate the phase boundaries. Single crystals of each of the phases were examined by x-ray diffraction with a precession camera and the unit cell dimensions and space group symmetry of the three ternary compounds are shown in table 1.

A tetragonal hollandite had been previous reported in this system by Ringwood (Acta Cryst. 1980, B36, 2913) and other hollandites have been reported in similar systems by Cadee (Acta Cryst. 1978, B34, 3534). Single crystals of hollandite grown from the primary phase field of the ternary system $BaO:Al_2O_3:TiO_2$ show much stronger diffuse scattering characteristics than do the hollandite crystals grown using a flux containing CaO and ZrO_2 (a mixture of hollandite, rutile, and zirconalite). Although the superstructure spots have stronger intensity they are still very diffuse and disk shaped rather than spherical.

Table 1. Unit Cell Data of Titanate Phases Synthesized During Phase Equilibria Studies of Ceramics for Nuclear Waste Encapsulation

Composition	Space Group	a	b	c	β	y*
$BaO \cdot 3Al_2O_3 \cdot TiO_2$	Pnnm,Pnn2	7.139	4.865	13.598		
$3BaO \cdot 5Al_2O_3 \cdot TiO_2$	C2/m,Cm,C2	15.754	11.341	4.985	109.5	
$Ba_xAl_{2x}Ti_{8-2x}O_{16}$ ($x \sim 1.23$-1.14)	I4/m,$I\bar{4}$,I4	9.94		2.920		8.122
$BaO \cdot MgO \cdot 3TiO_2$	C2/m,Cm,C2	15.208	3.899	9.109	98.5	
$BaO \cdot 6MgO \cdot 6TiO_2$	$P6_3mmc$	5.935		23.37		
$Ba_xMg_xTi_{8-x}O_{16}$ ($x \sim 1.33$-1.23)	I2/m,I2	9.920	2.992	10.256	91.5	8.528
$Cs_2O \cdot Al_2O_3 \cdot 2TiO_2$	Pbnn	9.973	5.480	9.025		
$Cs_xAl_xTi_{8-x}O_{16}$ ($x \sim 1.66$-1.33)	I4/m,$I\bar{4}$,I4	10.194		2.938		9.476
$Cs_xMg_{x/2}Ti_{8-x/2}O_{16}$ ($x \sim 1.45$)	I4/m,$I\bar{4}$,I4	10.278		2.970		

*Value of the modulation vector (in real space) for the incommensurate diffraction effect observed along the unique axis in the hollandite structure type.

Phase equilibria in the system BaO-MgO-TiO_2 was also examined, as a tetragonal hollandite phase has previously been reported in this system by Dryden and Wadsley (Trans. Faraday Soc. 54, 174, 1958). No tetragonal hollandite was encountered in the previously reported range of compositions, $Ba_x(Mg_xTi_{8-x})O_{16}$ ($1.14 \geqq x \geqq 0.67$) which had been synthesized by a Verneuil technique. However, a solid solution region of a monoclinic distorted hollandite structure was synthesized between 1:1:6 and 1:1:5 $BaO:MgO:TiO_2$ or $Ba_x(Mg_xTi_{8-x})O_{16}$ ($1.33_3 \geqq x \geqq 1.14_3$). The difference in composition and structure is unexplained at this time. Substitution of SrO for 10 mol percent of the BaO made little or no difference in the unit cell dimensions and symmetry. Reduction of the monoclinic phase by heating in N_2 at 1400 °C caused an increase in volume of the unit cell but little change in the amount of monoclinic distortion.

In addition to the hollandite, two new phases, never before reported, were encountered in the $BaO:MgO:TiO_2$ ternary system at the 1:1:3 and 1:1:6 composition. Single crystals of all three ternary phases were prepared from compositions determined to be in their primary phase fields as shown in figure 5. The unit cell dimensions and symmetry are also listed in table 1.

The single crystals of the hollandite phase were found to have unit cell dimensions similar to the end member of the solid solution with the maximum distortion and the maximum $BaO:MgO$ content corresponding to a composition of about 1:1:5. The superstructure found in these single crystals is the sharpest and most intense of any of the hollandite phases encountered in the present study. In addition the superstructure was found to be clearly incommensurate and not of exactly the value corresponding to the tripled $\underline{c}$ axis which had previously been suggested by Cadee.

High temperature x-ray diffraction powder patterns were obtained from the compositions 1:1:5, 1:1:5.5, and 1:1:6 $BaO:MgO:TiO_2$ as well as for the composition $0.9BaO:0.1SrO:1.0MgO:5TiO_2$. The monoclinic lattice of the hollandite-type was found to transform to tetragonal in all compositions. The transition temperatures in the $BaO:MgO:TiO_2$ compositions decreased with increasing TiO_2 content, ranging from about 265° ± 15 in the 1:1:5 and 1:1:5.5 specimens to 110° ± 10° in the 1:1:6 composition. The transition temperature in the $0.9BaO:0.1SrO:1.0MgO:5TiO_2$ specimen was apparently higher at about 340° ± 40.

The compound $BaMg_6Ti_6O_{19}$ is apparently isostructural with barium hexaferrite and, by analogy, can be called barium hexageikielite. No experiments have yet been conducted in this study in the system $BaO:FeO:Fe_2O_3:TiO_2$ but it may be predicted that the corresponding compound $BaFe^{+2}_6Ti^{+4}_6O_{19}$ (barium hexailmenite) is a stable phase in the system and probably forms a solid solution with $BaFe_{12}O_{19}$, barium hexaferrite. In the four component system $BaO:MgO:Al_2O_3:TiO_2$, a solid solution between barium hexageikielite and barium hexaluminate can be predicted, as well as the hollandite solid solution, with both Mg^{+2} and Al^{+3} in the framework. Both solid solutions should be equally useful host lattices for incorporation of Rb^+, Cs^+ and Sr^{+2} in nuclear waste ceramic systems.

To determine the amount of Cs^+ which could be incorporated in the hollandite structure, preliminary studies have been conducted in the systems $Cs_2O:MgO:TiO_2$, $Cs_2O:Al_2O_3:TiO_2$, and $BaO:Cs_2O:Al_2O_3:TiO_2$. The hollandite phase has been

previously reported by Beyeler and Schuler (Solid State Ionics 1, 77, 1980) to occur in the system containing MgO, but not in the ternary containing Al_2O_3. The single phase tetragonal hollandite structure was found to occur at approximately 1:1:10 in the Cs_2O:MgO:TiO_2 system or $Cs_x(Mg_{x/2}Ti_{8-x/2})O_{16}$ (x = 1.45). Another non-stoichiometric phase originally reported by Reid, Mumme, and Wadsley (Acta Cryst. B29, 1228, 1968) was also confirmed to exist in the system Cs_2O:MgO:TiO_2 at a ratio of about 1:1:4.7. However, x-ray powder diffraction patterns of specimens in the system Cs_2O:Al_2O_3:TiO_2 are very complex and could not be directly interpreted in terms of a hollandite phase corresponding to $Cs_x(Al_xTi_{8-x})O_{16}$.

Single crystals were obtained of a new phase corresponding to a compound at a composition $CsAlTiO_4$. The unit cell dimension and symmetry, given in table 1, together with the observation that this phase is pseudohexagonal, indicate that it probably has a structure very similar to $CsAlSiO_4$. There is no sign of the second phase found in the MgO system, even though this phase had originally been suggested to be present in the Cs_2O:Al_2O_3:TiO_2 system. Instead a tetragonal hollandite occurs, but in solid state preparations at one atmosphere of air, or in a sealed Pt tube, compositions between TiO_2 and $CsAlTiO_4$ are always three phases. A single phase hollandite can be synthesized by the application of a small amount of pressure at an as yet undetermined composition between about $Cs_xAl_xTi_{8-x}O_{16}$ ($1.66 \geqq x \geqq 1.33$). Apparently, at one atmosphere total pressure, there is a competition for the Ti^{+4} ion between 6-fold (TiO_2) and four-fold ($CsAlTiO_4$) coordination. Under these conditions the single phase hollandite cannot be synthesized and may be only metastable. It is apparently stabilized by a small amount of pressure. It may be predicted that a slight increase in the size of the impurity ion incorporated in the lattice will also stabilize the formation of the hollandite lattice and therefore solid solution with $Cs_xMg_{x/2}Ti_{8-x/2}O_{16}$ should increase the stability as would incorporation of the Ti^{+4} as the reduced ion Ti^{+3}. In the four component system, BaO:Cs_2O:Al_2O_3:TiO_2, it was found that in the hollandite lattice about 20 mol percent of the BaO could be replaced by Cs_2O with a corresponding increase of the Al_2O_3 content. Any additional Cs_2O content caused the phase $CsAlTiO_4$ to occur in the specimens prepared at one atmosphere total pressure. It can be assumed that a complete series of solid solutions can be prepared between $Ba_xAl_{2x}Ti_{8-2x}O_{16}$ and $Cs_xAl_xTi_{8-x}O_{16}$ by the application of a small amount of total pressure.

Ceramic samples were preapred for AC impedance measurements from the following compositions: BaO:Al_2O_3:$4.5TiO_2$, $Ba_{0.5}Sr_{0.5}Al_2O_3$:$4.5TiO_2$, $Ba_{0.9}Sr_{0.1}Al_2O_3$:$4.5TiO_2$, $BaO_{0.9}Cs_2O_{0.1}$:Al_2O_3:$4.5TiO_2$, $BaO_{0.9}K_2O_{0.1}$:Al_2O_3:$4.5TiO_2$, and $Ba_{0.9}Sr_{0.1}Al_2O_3$:$4.5TiO_2$. The ceramic pellets were generally all about 86 percent theoretical density. In addition the oxidation of partially reduced BaO:Al_2O_3:$4.5TiO_2$ hollandite was examined as a function of different temperatures in air and pure oxygen.

The phase equilibria results were utilized to synthesize single crystals of the various phases encountered in ternary and quaternary combinations within the Cs_2O-BaO-SrO-MgO-Al_2O_3-TiO_2 system. All crystals of incongruently melted phases were grown by very slow cooling of compositions within the primary phase field of the desired compound. Only for the Cs-Al-Ti hollandite phase was it necessary to use an additional flux. In this case a small amount of CsF was sufficient to enable small single crystals to be grown in sealed Pt tubes.

A survey was made of pertinent phase equilibria diagrams to determine if enough data were available in the literature for a compilation to be prepared of "Phase Diagrams for Ceramists Pertinent to Nuclear Waste Management." In addition to searching Volumes I through V of "Phase Diagrams for Ceramists" several computer searches were undertaken using Chemical Abstracts, DOE Reports, etc. The total number of published phase diagrams specifically applicable to the glass and ceramic compositions suggested for nuclear waste encapsulation were limited to only about five to six diagrams, mostly of simple binary or ternary systems. Most of the pertinent diagrams have not been studied in enough detail to have appeared in the literature. It may, therefore, be concluded that the study of phase diagrams of the type reported in this section is very important in order to determine the phases which may be expected to occur in ceramic systems in which the "tailoring" or compositions is inexact due to inexact knowledge of the real composition of the waste.

Thermochemistry of Slag
Subtask 4 of Task 12151

L. P. Cook

Studies on the phase equilibrium behavior of the system K_2O-CaO-Al_2O_3-SiO_2 were continued, with the aim of establishing, as definitely as possible, subsolidus phase equilibria among eleven crystalline compounds. Once this is done, thermodynamic data for the solids may be used to develop a phase-equilibrium-derived model for calculation of potassium vapor pressures over quaternary melts. These melts simulate a wide compositional range of MHD slags produced by combustion of western coal. Three types of subsolidus experiment have been performed: glass crystallization experiments, 1000 h equilibrations, and solid state reactions using alternative combinations of phases. Previously hypothesized phase relations were confirmed, and solid solution among phases is negligible, with the possible exception of $KAlSi_2O_6$ which exhibits substantial K_2O-deficiency. Thus it appears that development of an accurate power series model for calculation of quaternary activity coefficients from phase equilibrium data is feasible. The solution to the quaternary formulation of the Gibbs-Dubem equations has been derived and a least squares fit of polynomial coefficients will be attempted. If the fit is successful the model will be tested and refined.

In a related effort, the attempt to model K_2O-CaO-Al_2O_3-SiO_2 liquidus surfaces continued and preliminary results were presented at the 1981 Spring Annual Meeting of the American Ceramic Society in Washington, D.C. A quasichemical approach to melt polymerization was used which allows quantitative calculation of proportions of silicate structons. From this information it is possible to calculate activities and, from these, to calculate liquidus surfaces. However, it was necessary to first develop a proper treatment of aluminum in these four-component melts. It does not appear possible to develop a general solution model for aluminum as a calcium aluminate species. Currently the most success at fitting liquidus data has been achieved using a species containing approximate three aluminum atoms; possibly this is a positively charged species. Similarly most precipitation reactions appear to require silicate species with three to five or more silica atoms. Furthermore, the model works best if potassium aluminate species with multiplicity of more than four are assumed. The best model thus currently available requires a rather complicated set of assumptions,

but conversely leads to interesting and rather specific conjectures about melt structure. It should be pointed out that thermodynamic and phase equilibrium data input to this model consist of data from seven relatively well-studied binary joins. It appears that the possibility for use of this model over a broad range of compositions is encouraging. The best accuracy at present is ~ 50 °C and ~ 10 mol percent. Refinement of the model, with experimental feedback, will be continued through the end of the fiscal year, and if time permits comparison with other solution models will be attempted.

Among the directly applicable results of research on slag thermochemistry are a first-order assessment of silicates as MHD-slag resistant refractories. Potassium aluminosilicates are expected to have optimal corrosion resistance and a preliminary description of the processing science, properties, and suitability of some of these materials as thermal insulators in MHD systems was given in a paper presented at the 19th Symposium on Engineering Aspects of MHD (1981) in Tullahoma, Tennessee. Another material with potentially high potassium corrosion resistance at lower temperatures is anorthite. Furthermore, it can be sintered to produce dense ceramics. Preliminary studies of processing science, and microstructure of anorthite ceramics have been made, including the application of SEM, TEM, and STEM methods.

Materials for Fluidic Capillary Pyrometer (FCP) Sensors
Subtask 5 of Task 12151

T. Negas

The fluidic capillary pyrometer (FCP) is a device consisting of a probe containing a variable fluid resistor, normally a capillary, whose resistive properties are proportional to fluid (a gas) viscosity and, hence, to temperature. An external pressure sensing circuit measures resistance changes as a function of temperature when gas flow is laminar. Development of this method to measure temperature is relatively new but has advanced rapidly most recently.

In cooperation with Harry Diamond Laboratory researchers, this subtask has been concerned with (1) the development of new designs and fabrication methods for FCP sensors, (2) the development and/or selection of FCP construction materials necessary for specific high temperature applications, (3) the fabrication of FCP sensors in cooperation with private industry, (4) the calibration (not certification) of sensors for T > 1200 °C, and (5) the testing of sensors in environments simulating actual practice.

A new design useful for refractory metals which are difficult to machine to provide an internal capillary was demonstrated and tested. A patent application was filed. The invention recognizes that a capillary-like resistance does not require a constant or a regular shape cross section. A crushed tube, wherein the gas flow is maintained very low through the resultant small cross-sectional area, behaves exactly like a capillary in that the pressure drop is directly proportional only to viscosity when volume flow is constant. In a corollary manner, at constant temperature and, hence, viscosity, the relationship for low flows between pressure drop and flow is linear. Figure 6 illustrates a typical FCP calibration obtained for a crimped molybdenum tube placed within a larger Mo-tube

having one end closed. Nitrogen was the working fluid which passed through the crimp and exhausted by the annular passage formed by the outer tube. Fabrication was accomplished by manually deforming the end of an open-end tube. To determine the amount of crushing necessary, a pressure P_{out} is applied to the tube end through a fluid resistor of known R_F. P_{out} is related directly to the amount of flattening of the tube, R_C, by:

$$P_{out} = P_S/R_F/R_C$$

When P_S and R_F are fixed, P_{out} is a direct measure of R_C. Thus, the tube is crushed until P_{out} is at a predetermined value.

Testing of monolithic, ceramic-based FCP probes containing capillaries at the sensing head were completed. Alumina probes, previously fabricated and calibrated during this program, were used with air as the working fluid. Over 5000 hours of continuous operation were accomplished within a U.S. Army rotary hearth forging furnace (1200 to 1300 °C) and nearly one year of operation within a commercial periodic kiln used to sinter ceramics (1200 to 1550 °C). A comparison of pre- and post-test pressure versus flow characteristics obtained at room temperature (e.g., figure 7) indicated that within experimental error the capillaries did not deteriorate.

A collaborative effort among NBS, HDL, and the Sandia Laboratories (Albuquerque) was initiated to measure the temperature of a simulated nuclear melt-down. The Sandia Labs have constructed a massive, inductively heated furnace to conduct experiments which can simulate a nuclear melt-down. Their goal is to melt a UO_2/La_2O_3 mixture within a 90 percent Ta:10 percent W (~ 2' o.d. x 3' length) contained within a graphite susceptor. Temperature (to ~ 2600 °C) cannot be measured by pyrometry or by thermocouples. Thus, the FCP is an attractive method. Experiments have been designed so that the system is tested at progressively higher temperature. The first phase was completed successfully and involved the measurement of temperature (~ 24 h) within the graphite susceptor to ~ 1800 °C, without a crucible. For this we merely used an available alumina probe to demonstrate feasibility. The second phase will include the crucible and a melt of TiO_{2_x} (1800 to 1900 °C). Molybdenum FCP probes are under construction to measure temperature in the oxide melt. The third phase will be the final test to 2600 to 2700 °C. For a variety of reasons, Ta 10 percent W or Ta coated with W are the candidate FCP construction materials. Several design features were incorporated in the system by Sandia researchers to retard diffusion of and corrosion by carbon from the susceptor for these materials. However, two problems remain. First, the UO_2/La_2O_3 melt will generate a substantial oxygen partial pressure, possibly in the 10^4 atm range or higher. Therefore, the metal probe will be subject to wastage via vapor phase oxidation/transport but at a rate as yet undefined. Second, calibration of the probe above ~ 2300 °C may prove difficult but methods are under discussion with other groups at NBS.

Work has also continued on the development of FCP probes for continuous (to 8 h) temperature measurement in molten iron heated inductively. Numerous tests have been conducted using Mo-based probes coated with oxides and composites applied by the arc plasma spray (APS) method. This has been a cooperative effort among NBS, HDL, and APS Materials, Inc. Spinel ($MgAl_2O_4$) and $ZrO_2(MgO)$ are candidate oxides while Mo or $MoSi_2$ are materials included in the composites. Processing problems, however, were encountered for the $MoSi_2$ coatings. During

arc plasma spraying (APS), it appears that Si vaporizes preferentially from the $MoSi_2$ feedstock. The resulting deposit consists of Mo, Mo_5Si_3, and Mo_3Si without free Si or glassy SiO_2. The microstructure is heterogeneous although relatively dense. APS process parameters, including different powder feedstocks, require better definition to obtain uniform, single-phase $MoSi_2$ deposits. Alternatively, other coating techniques (see below) may be necessary.

Despite, these fabrication problems, coated Mo-based sensors survive up to ~ 2 h in molten iron at 1500 to 1550 °C. Failure is always at the melt/air interface where a fluid, corrosive slag containing oxides of iron, manganese, and silicon develops. All coatings are fluxed by this slag until the Mo is exposed to alloy with the molten metal. Subsequently, ceramic castables (Al_2O_3- and MgO-based) were applied to coated Mo sensors at the anticipated slag line. These serve as sacrificial materials to extend lifetime to within eight hours but do not hinder the response time of the sensor tip within the metal melt.

Future work will involve the completion of cooperative efforts with Sandia and the development of fabrication and processing methodology for fast response, less massive, ceramic-based probes.

Reactions of Si_3N_4 and Metals
Subtask 6 of Task 12151

J. L. Waring

This project is a portion of a program to investigate corrosive resistant coatings on metals for use in fluidic sensor applications. The approach was to survey some systems by investigating the chemistry of oxidation resistant silicide coatings on materials of interest to the refractory metal industry, i.e., Mo, Ta, W, Nb, Zr, and Hf and to the ferrous metal industry, i.e., Fe, Cr, Co, and Ni.

The first system that was investigated was Si-Mo-N_2. A tentative phase diagram is given in figure 8. This diagram represents an isothermal cut at 1600 °C and 10 psig of 95 percent N_2 - 5 percent H_2. In essence, compositions falling on the join between Mo and Si_3N_4 up to the compositional line Mo_5Si_3-N_2 form final reaction products occurring along the Mo-Si binary. Starting compositions in the triangle Si-Si_3N_4-Mo_5Si_3 combine with N_2 and form reaction products with compositions along the join Mo_5Si_3-Si_3N_4. Some of the experimental results in this portion of the system appear to be inconsistent and additional experimentation is needed.

From the phase diagram it can be seen that Si_3N_4 is not stable with Mo in the presence of 95 percent N_2 - 5 percent H_2. It follows that Si_3N_4 may be used as a precursor for the deposition of thin protective films of silicides on Mo. Small coupons of Mo were encapsulated with Si_3N_4 and heated to about 1600 °C for various periods of time to accelerate diffusion of Si. Thin films of molybdenum silicide phases were grown. These results are shown in tracings of SEM photographs (figure 9). In the first tracing it can be seen that Mo_3Si and Mo_5Si_3 are formed on Mo at a thickness of 17 μm in 30 minutes. The second and third tracings of 1 and 2 h experiments show the same phase formation of 35 μm and 70 μm, respectively. From the above it would appear that the rate of formation is linear at about 35 μm/h.

Some preliminary reaction experiments were conducted in the system Si-Ta-N. Two specimens of Ta + Si_3N_4 were heated at 1620 (19 h) and 1403 (2-1/2 h) in one atmosphere 95 percent N_2 - 5 percent H_2. In the first reaction Ta_5S_{13} and TaN were formed in the second TaN, Si_3N_4 and an unknown phase were formed. This system is more complex than the Si-Mo-N system and will require considerably more investigation. In the system Si-Fe-N_2 one specimen of Fe + Si_3N_4 was heated to 1350 °C (20 h) in 95 percent N_2 - 5 percent H_2. The results were not definitive although the x-ray pattern showed a solid solution phase with a composition about Fe_3Si.

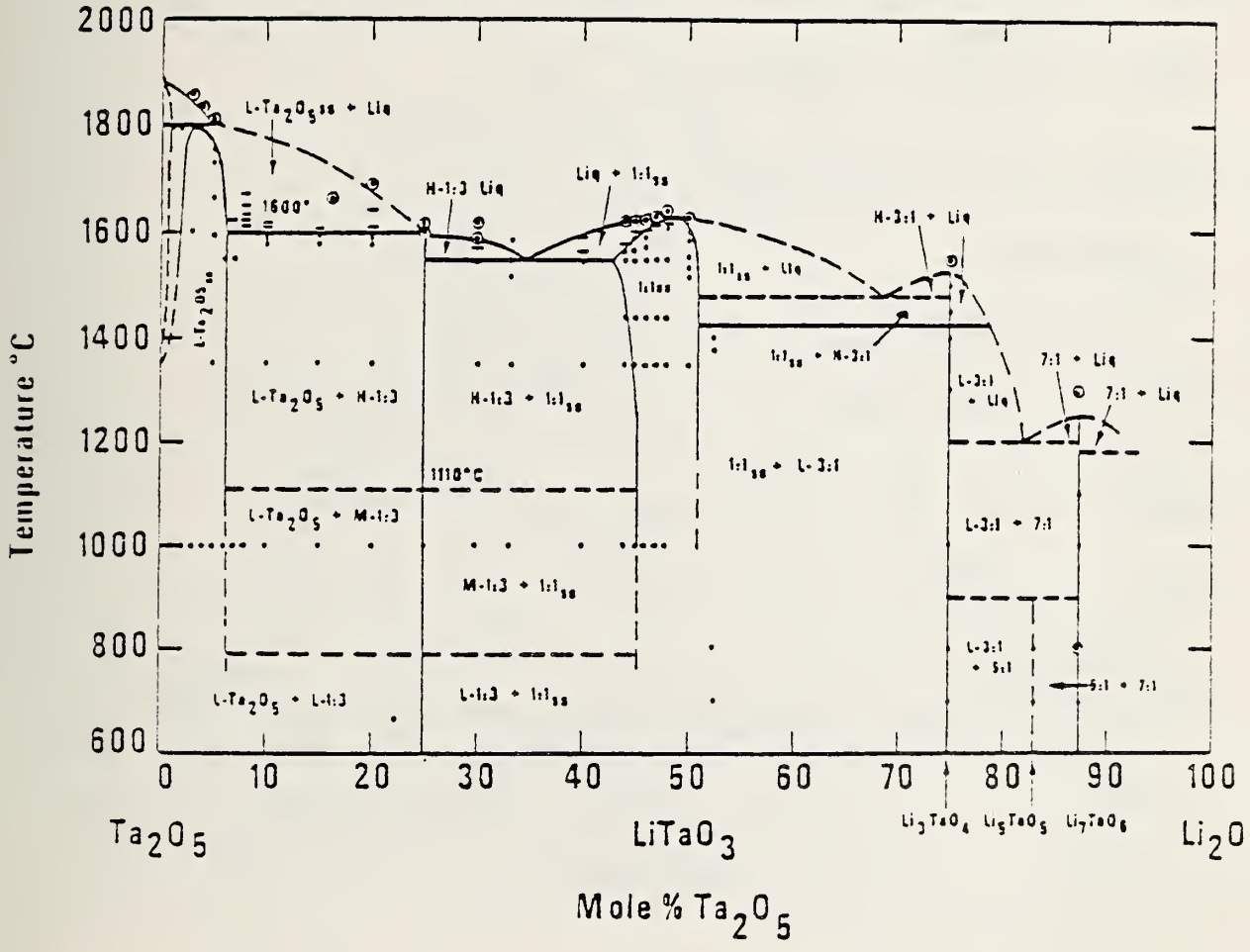


Figure 1. Phase equilibria diagram for the binary system Li_2O-Ta_2O_5

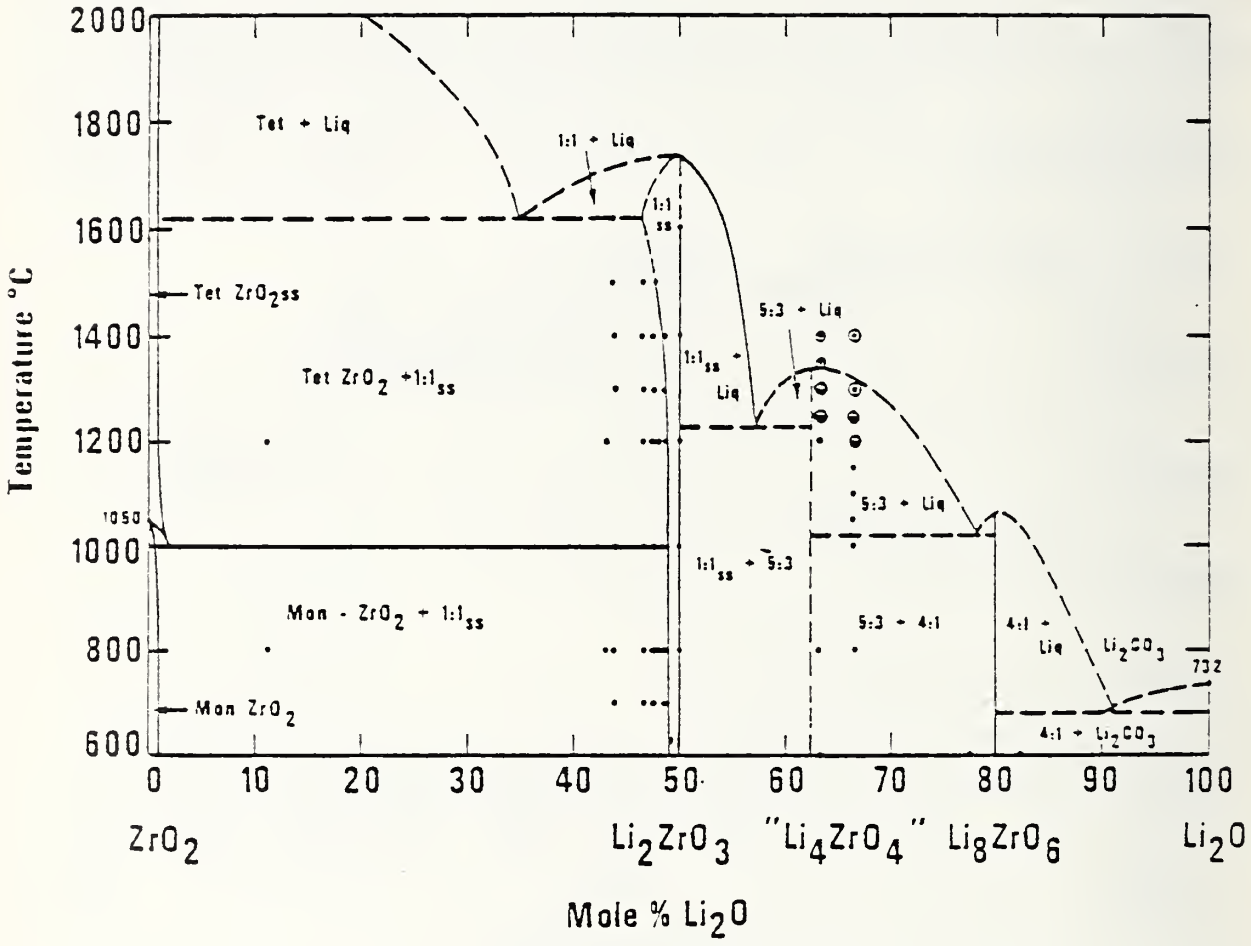


Figure 2. Phase equilibria diagram for the binary system Li_2O-ZrO_2

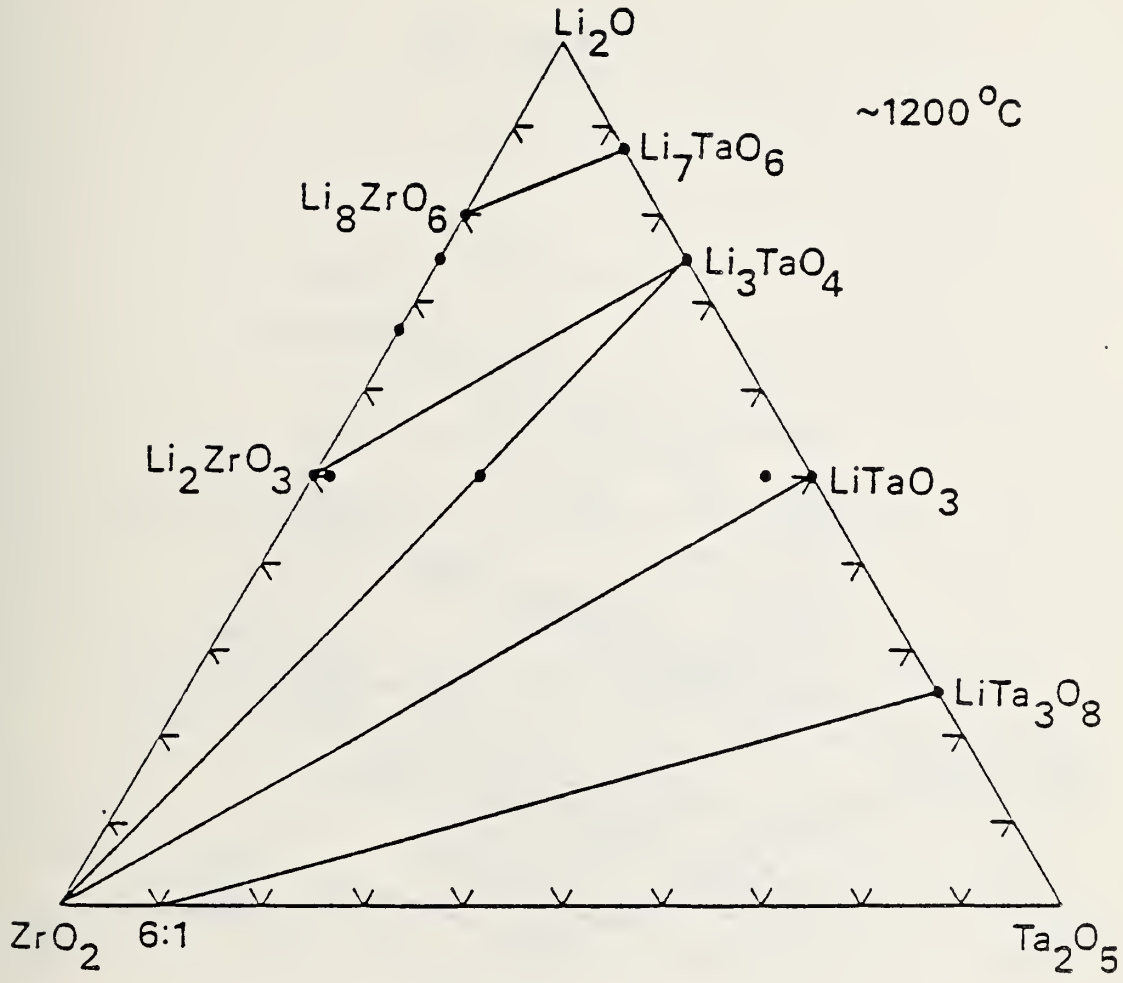


Figure 3. Compatibility triangles for the ternary system Li_2O-ZrO_2-Ta_2O_5.

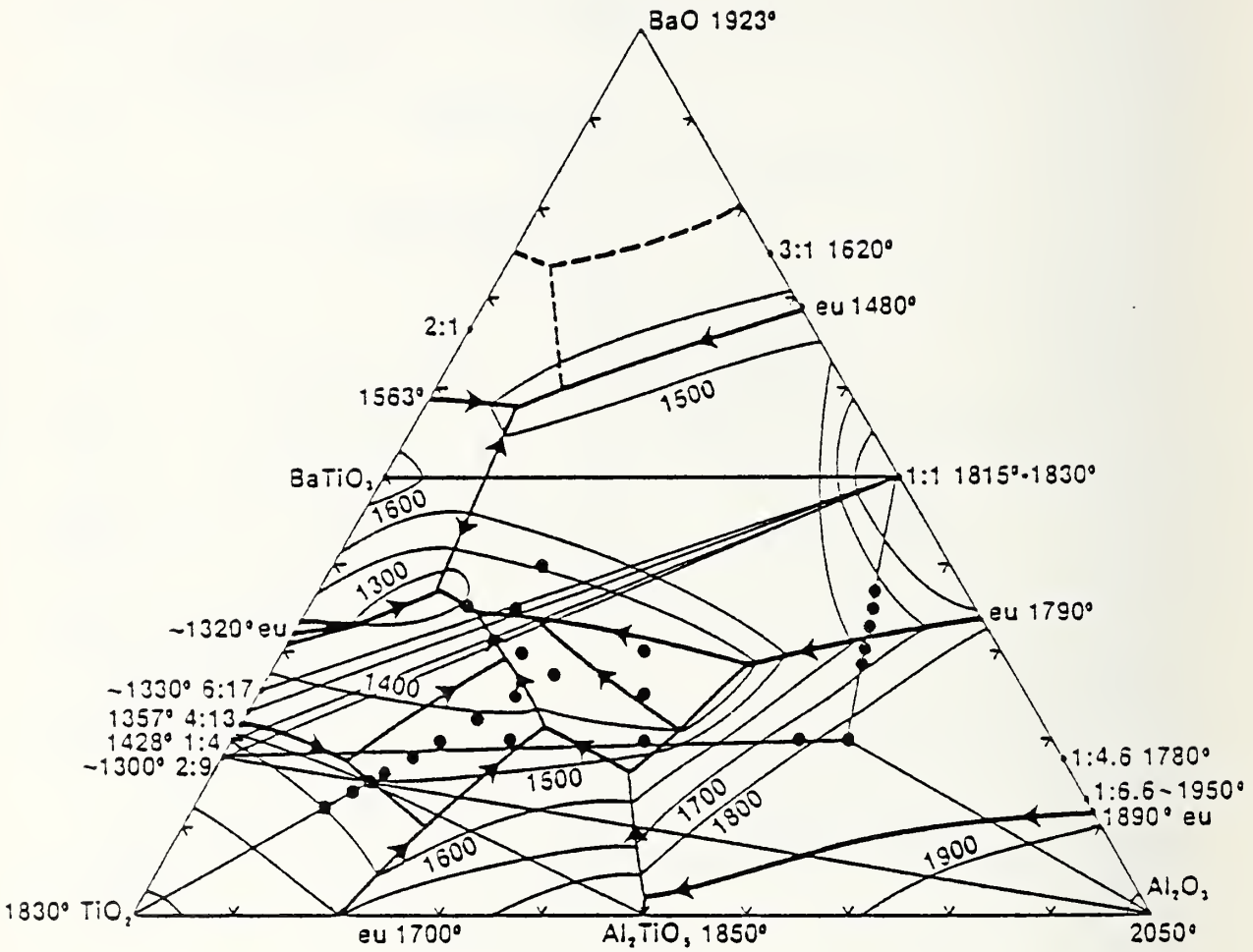


Figure 4. Phase equilibria diagram, consistent with limited experimental data, for the ternary system $BaO-Al_2O_3-TiO_2$.

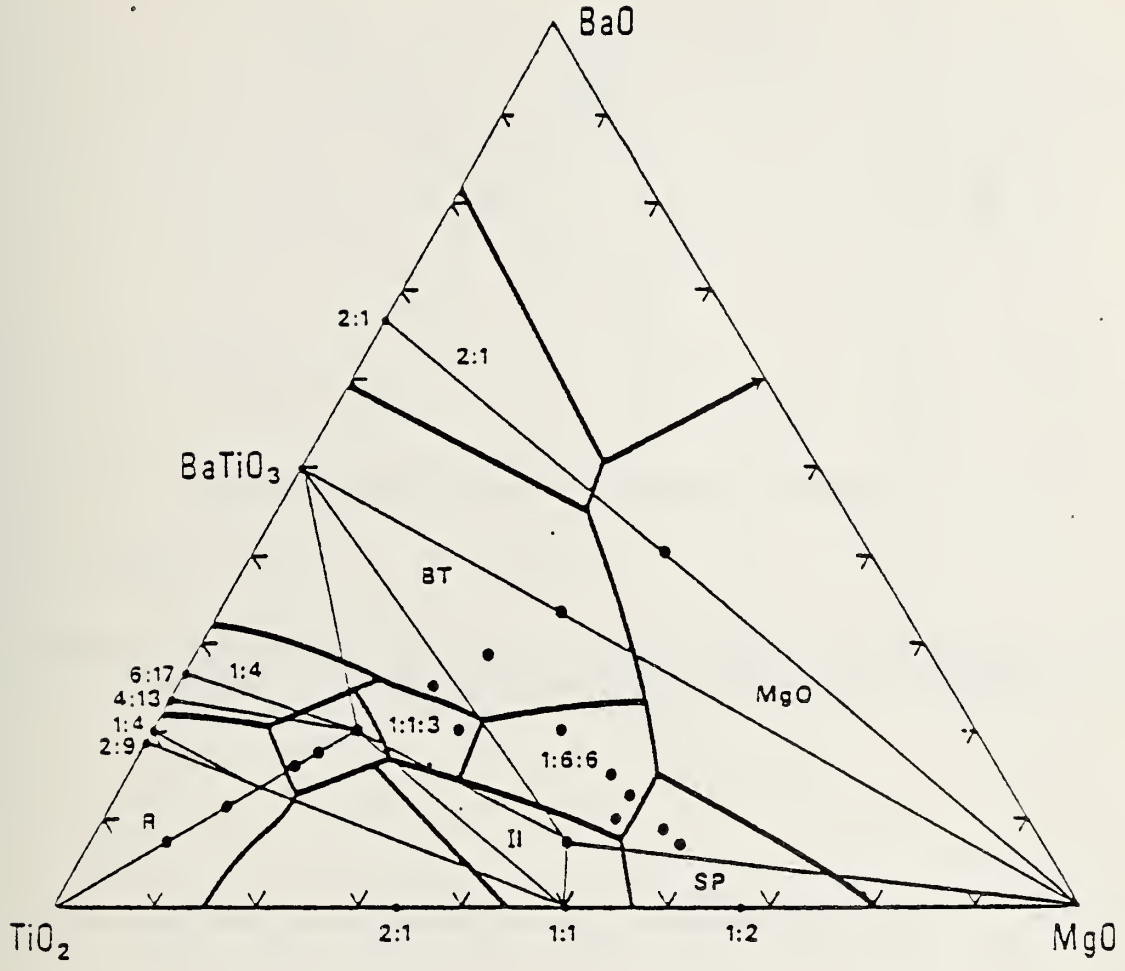


Figure 5. Phase equilibria diagram, consistent with very limited experimental data, for the ternary system BaO-MgO-TiO_2.

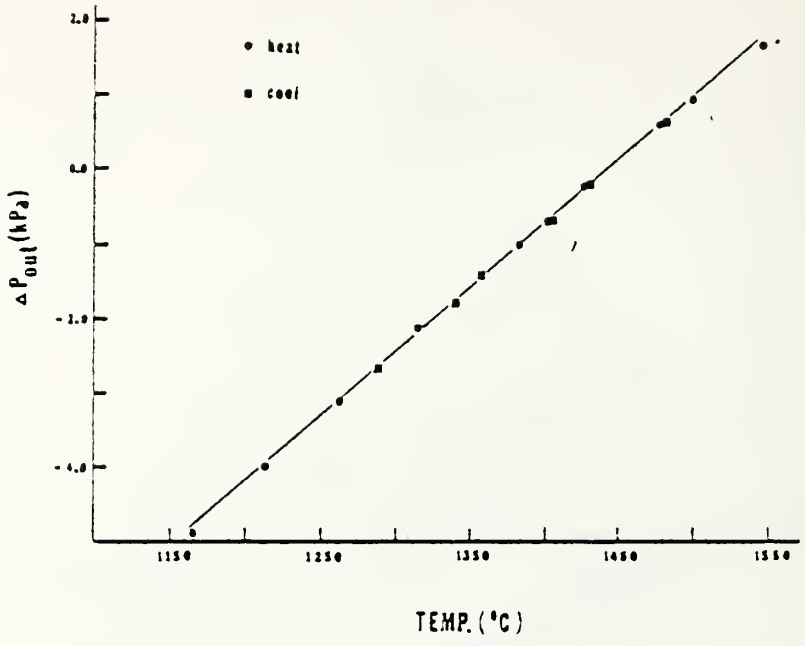


Figure 6. Typical fluidic capillary pyrometer (FCP) calibration obtained for a crimped Mo tube with a large Mo tube (working fluid--N_2).

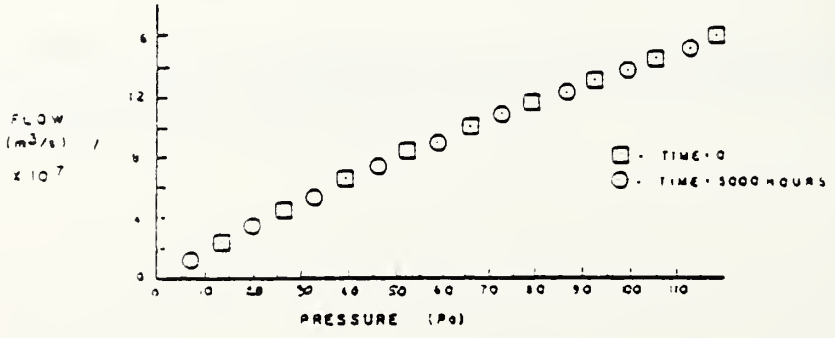


Figure 7. Pressure versus flow characteristics for monolithic, ceramic based (alumina) FCP probes.

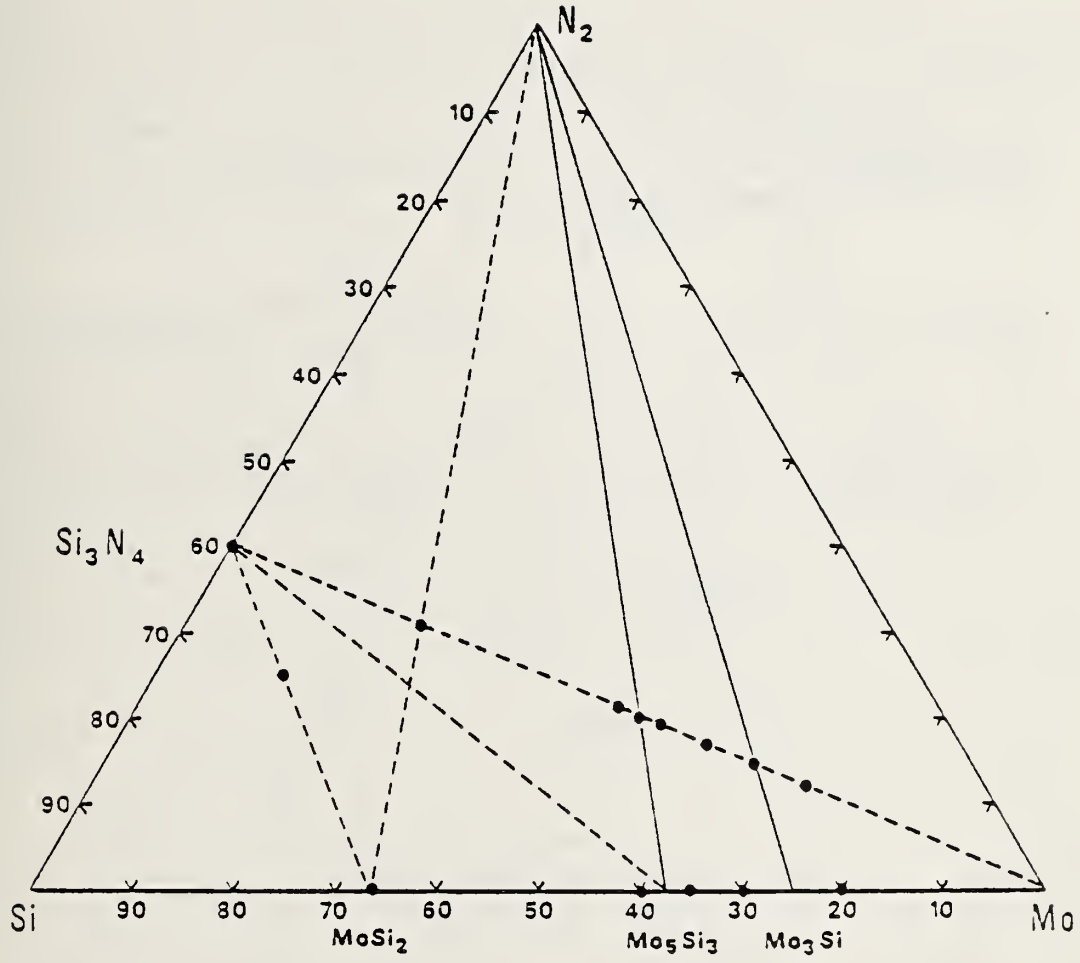


Figure 8. Compatibility triangles for the ternary system Si-Mo-N_2 (1600 °C - 10 psig N_2 - 5 percent H_2)

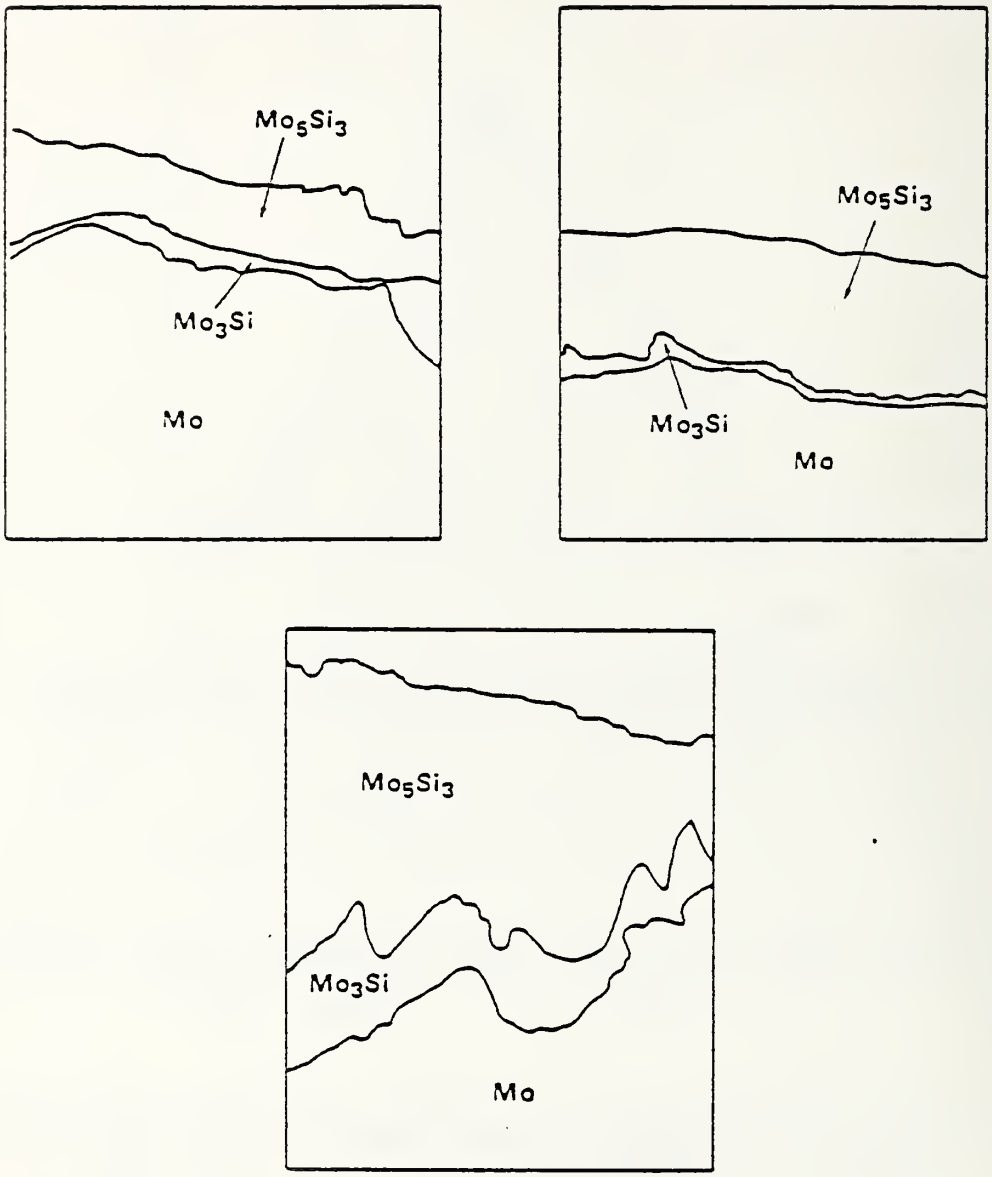


Figure 9. Silicide castings on Mo metal cupons embedded in Si_3N_4 and heated to 1600 °C. (a) 30 minutes, (b) 1 hour, (c) 2 hours.

STRUCTURAL METHODS FOR PROCESSING, MANUFACTURING, AND DURABILITY
Task 12153

The objective of Task 12153 is to contribute to materials research by applying the methods of x-ray diffraction to identification, characterization, and quantitative analysis of crystalline and amorphous materials. Measurements are carried out at high pressures and at both high and low temperatures as well as at ambient conditions. An important aspect of the work is the support provided to other organizations in the form of standard reference data, standard reference materials, data compilations, measurement methods and practices, computer algorithms, and improved instrumentation.

The outputs of this task are being applied to the needs of a number of Government agencies. Power plant ash formed under various conditions of combustion is being characterized before and after leaching in collaboration with the Laramie Energy Technology Center of DOE. The data obtained will be useful for the development of an ash management program, including quality control to permit utilization of by-products. In an attempt to develop a comprehensive mathematical model for leach test measurements of radioactive solid wastes, a detailed numerical analysis of the chemical reaction/deposited-layer-flaking problem is being performed for the DOE Office of Nuclear Waste Management. The results emphasize the need for examining the details of chemical reactions at the solid-solvent interface if reliable leach test measurements are to be made. The oxidation of commercial silicon carbide ceramics is being studied under a contract with DOE. An improved understanding of microstructural and mechanical behavior of structural ceramics for heat engines and heat recovery systems is being sought. A data center is being operated cooperatively for DOE to provide a central data base on materials and components for fossil energy applications. Computer storage and access is under the control of a commercial data base management system. A study of the preparation and characterization of CdS and its physical properties at high pressure is being carried out to help scientists at the Watervleit Arsenal explain anomalous magnetic properties of material pressure quenched from above the semi-conductor-conductor transition. The JCPDS International Centre for Diffraction Data continues to maintain research associates at NBS who collaborate with scientists in Division 565 to obtain data on additional materials for the Powder Diffraction File and to improve the accuracy and validity of data already in the file.

A new technique for obtaining powder diffraction patterns from small samples in confined systems such as the diamond anvil pressure cell has been tested at the Cornell High Energy Synchrotron Source (CHESS) in collaboration with Professor B. W. Batterman and others from Cornell University. In a collaborative effort, nearest neighbor O-O distances in ice VII were determined by energy dispersive powder diffraction at pressures up to 36 GPa and used in the interpretation of the Raman OH-stretching frequencies measured by Professor G. Walrafin of Howard University. A very successful collaboration with Professor I. Fujishiro, a guest worker from the University of Nagoya, resulted in studies of the pressure dependence of viscosity and the glass transition pressure of binary and ternary systems used to provide a hydrostatic environment in high pressure experiments. As a result of this work, the hydrostatic range accessible for experimentation has been increased by 40 percent. More details about each of the programs under Task 12153 are presented below.

Powder Diffraction
Subtask 1 of Task 12153

C. R. Hubbard

The objectives of this subtask are to improve measurement capability and analysis of x-ray powder diffraction data for production of SRMs, collaboration with the JCPDS Research Associateship and development of quantitative phase analysis methods and to improve the quality and utility of the Powder Diffraction File. Activities include: automation of x-ray powder diffraction data collection; computer data analysis of powder patterns; development of quantitative phase analysis capability for crystalline and amorphous content; certification of SRMs; investigation of crystallite size and residual strain determination; guiding the JCPDS Research Associateship's determination of Standard Patterns; and participation in JCPDS committees.

Automation. Powder diffractometer automation is a fundamental development to support improved measurement capability and to support other agency programs. AUTO, a real time, multi-instrument, intelligent data collection program, was written last year. Since then an NBS Internal Report was written as documentation and as a user's guide. Since AUTO's initial writing the need for several new features became obvious. To improve the quality of peak height intensity data a "peak-find" routine was written. This routine directs rapid data collection from 0.12 deg 2θ below the expected peak position to 0.125 deg 2θ above in steps of 0.005 deg 2θ. The 50 data points are smoothed using a 13 point Savitsky-Golay smoothing algorithm. The maximum in the smoothed data is taken as the peak location. This algorithm overcomes problems due to sample displacement effects on peak position.

Installation and interfacing of a sample changer and sample temperature monitor are underway. Both devices will be controlled through the NBS BUS instrument interface. The interface cards were completed on July 30, 1981. To implement the associated software, AUTO was overlayed. Approximately 20 K bytes of memory are now available for new routines and enhancements. Implementation of subroutines to (1) read the sample temperature and (2) control a sample changer are underway.

File transfer to the Univac 1108 for data processing is still being performed via floppy disc. While the NBS NET connections are in place, the necessary net driver software is not yet available from the Scientific Computing Division.

Computer Analysis of Powder Patterns. The goal of this activity is to automatically analyze the recorded digital data for peak position and intensity with improved precision and accuracy. Processing of powder data collected digitally requires many independent algorithms to be integrated into a complete package. Use of the Automatic Data Reduction (ADR) package from Alfred University exhibited several critical failings for routine use at NBS. In particular, the determination of the background level often failed, and the profile refinement code, which was known to be weak, often produced spurious results. To overcome these deficiencies, N. Panagiotopoulos (JCPDS-Research Associate) has developed a new program which determines regions of background from the fluctuations of the second derivative. Regions not considered back-

ground are considered peak group regions. Trial peak location, intensity, and breadth are then obtained for each peak within a peak group. Finally, the parameters of the peaks are refined.

We have investigated profiles of the form $P/(1 + ax^2 + bx^4 + cx^6)$ where P is the peak height and $x = 2\theta - 2\theta_0$, with $2\theta_0$ the center of the peak. This model is a generalization of a series expansion of form the P exp $[-ax^2]$. In particular, profiles of the simpler form $f(x) = P/(1 + ax^2 + bx^4)$ have been studied extensively. This form reduces to a Lorentzian for a = 2b. To account for the observed profile the parameters P, $2\theta_0$, a and b are adjusted with a simplex refinement routine. For asymmetric profiles two pairs of a and b are used to describe the high angle and low angle portions of the profile. A typical fit to raw data is shown in figure 1. The calculation of these profiles with computers is about 50 times faster than profiles such as the Pearson Type VII, which contain exponential factors. Their use results in an appreciable reduction of the cost of fitting the data. For overlapping groups, cyclic refinement, one peak at a time, of all peaks within a peak group was found to be necessary to improve the accuracy of parameters of weak peaks. Initial results of profile refinement using the simpler symmetric modified Lorentzian were very encouraging. For profiles measured to a net intensity of 10,000 counts, the RMS deviation [2θ (obs)-2θ (calc)] for several samples was about 0.005° 2θ. This is approximately three times better than results obtained from our best strip chart recorded patterns. Further improvements, particularly in regions of overlap, are to be expected with the newer profile function. Tests on the accuracy of intensity measurements are given in the next section.

Quantitative Analysis--Crystalline Phases. Quantitative phase analysis by x-ray powder diffraction is being rediscovered by industry because of their need for improved characterization of starting materials and final products. The recent introduction of computer controlled powder diffractometers has also enabled quantitative analysis measurements to become routine. Philips Electronics indicates that over two-thirds of all new diffractometers being sold in the U.S. are automated instruments intended for quantitative analysis. The NBS effort is intended to support other agency projects and to advance the state-of-the-art. The system of programs POWDER*QUANT written last year by C. R. Hubbard and R. L. Snyder (Alfred University), has undergone testing, revision, and enhancement in the last year. The revisions involved generalization of code in order that the algorithms are as free of author-imposed limitations as possible. In addition, the programs are written in FORTRAN 77 for ease of transportability. Array dimensions are set by global PARAMETER statements which also enhances portability. A user's guide has been drafted and will be issued as an NBS Internal Report.

A major addition to the system is the program RUNFIL which processes data collected on standards and produces a run file for AUTO. The generated run file contains the required quantitative constants for either the internal standard or the intensity ratio method of analysis for all the phases expected in a mixture. Generation of a run file for quantitative analysis of a multiphase mixture is now a simple procedure. Program RUNFIL also incorporates capability to determine relative intensities and reference intensity ratios.

Throughout all programs in POWDER*QUANT, particular attention has been paid to error analysis. In the recommended approach, multiple lines of the standard and multiple mountings of the sample are used. Counting statistics are used for weighting of averages. These procedures are particularly useful when care is taken to prepare orientation-free samples.

A spray-drier has been built and tested which provides an excellent means to prepare orientation-free samples of phases stable to ~ 150 °C. The spray-drier consists of a nozzle and a heated chamber. A slurry of sample, binder, deflocculant and supension medium (often H_2O) is siphoned through the nozzle by a steady flow of air. The resultant droplets dry before hitting any surface of the chamber, yielding 30 to 50 μm aggregate spheres of the sample. These spheres exhibit random orientation of the constituent crystallites. Recovery is approximately 50 to 75 percent. Quantities as small as 1 g may be spray dried. To test the entire quantitative analysis scheme (sample preparation, data collection, and data analysis) spray-dried mixtures of silicon + titanium diboride and silicon + alumina were prepared ranging in compositon from 5:95 to 90:10 by weight. The Si + TiB_2 mixture contains a highly absorbing phase and was used to evaluate microabsorption effects. Both mixtures were prepared at Alfred University and are being studied by SEM to assess the homogeneity of the spray-dried spheres. X-ray powder diffraction data for the twenty samples was collected and analyzed at NBS. The nine spray-dried mixtures of Si + Al_2O_3 yielded exceptionally precise results. A total of six α-Al_2O_3 and three Si peaks were integrated to a target counting precision of 0.5 percent subject to the contraints of 15 minutes maximum time. A couple of the mixtures were measured to 1.0 percent/10 minutes, and a couple to 0.25 percent/20 minutes. Data for each sample were measured two to four times. Altogether, each line was measured 28 times. The derived relative intensities for each of the lines have an RMS deviation of ≦ 0.5 percent. This represents the results of measurements on low-to-high concentration and medium-to-strong relative intensity lines. The 18 possible pairings of α-Al_2O_3 lines with Si lines for each of the 28 sets of data were used to calculate the Reference Intensity Ratio. The overall average of I/I_c was 3.440 with an RMS deviation over the 504 line pairs of 0.005. This level of precision has never been reported for x-ray powder diffraction measurements. The values are at least a factor of five times more precise than our previous best results for relative intensities and I/I_c measurements.

In addition, the estimated standard deviations (E.S.D.) derived from propagation of counting statistic errors agree well with the RMS deviation. A small, possibly significant, trend of I/I_c with concentration of α-Al_2O_3 was detected. Similarily excellent results were obtained for the eight Si + TiB_2 mixtures. No concentration dependence was observed even at the 5 wt. % Si level.

Quantitative Analysis--Amorphous SiO_2. Quantitative analysis of an amorphous phase in the presence of crystalline phases has been generally unattainable particularly in system such as glass + αSiO_2. Results of this activity will be applied to analysis of glass content in fly ash. A spiking method of analysis has been shown to be the superior method for analysis of amorphous SiO_2 content in the presence of crystalline α-SiO_2. In this technique regions of the amorphous halo are integrated. Background from pure Si powder is used

as an approximation for the instrumental background in the integrated regions. A test mixture containing no amorphous SiO_2 was analyzed by the spiking method. The calculated concentration was -2.1 percent with an E.S.D. of 0.9 percent. The fact that this is within 3 E.S.D. of zero concentration indicates that low concentrations of amorphous SiO_2 in quartz can be determined.

A pattern summation technique for determination of amorphous SiO_2 was also tested. It was found to be quite sensitive to effects of preferred orientation. This technique may be useful with spray-dried samples.

Standard Reference Materials--D-Spacing Standards. Accurate measurement of peak 2θ values has been shown to be critical in the qualitative analysis of multiphase mixtures using the Powder Diffraction File. Accurate 2θ's are also required for accurate lattice parameter determination. Internal standards are well known as the best procedure for obtaining high accuracy on a routine basis. NBS has supported development of two SRMs to be used as internal standards. Material for a large d-spacing SRM, fluorophlogopite, has been selected and certification is under way. This materials exhibits very sharp diffraction profiles and orients when pressed. The diffraction pattern exhibits principally only 00ℓ type reflections, with the largest d-value $\approx$9.97Å. The profile fitting procedures described above will be used to accurately determine the $\underline{c}$ lattice parameter. Tests for stability of the synthetic mica included heating at 150 °C for 6 h, boiling in water for 8 h followed by air drying, and exposure to x-radiation for 24 h. No change in the lattice parameter was observed. Certification was completed September 30, 1981.

Nearly all of SRM 640, silicon powder, has been sold and recertification of approximately 7 kg of powder saved from the earlier effort is under way. We are reducing the average particle size to < 10 μm. Tests show that this will eliminate occasional profile distortion due to large grains and will make the SRM more useful. Classification into a course fraction and a fine fraction using a zig-zag classifier has been completed. The course material was sent out for jet milling in April 1981 after which it will be blended with our fines. Powder patterns of randomly selected samples will be measured using AUTO, and analyzed by CALIB. Lattice parameters obtained by least squares refinement will be corrected to 25 °C. These procedures have been tested with existing SRM 640 Si powder and with Si powder provided by Chinese scientists. Interestingly, the Chinese Si had a significantly larger lattice parameter than does SRM 640.

Standard Reference Materials--Quartz Powder. Respirable quartz is a common industrial hazard. Many industrial laboratories are required by NIOSH to monitor the level of respirable quartz. The procedures involve collection on filters and quantitative analysis by x-ray powder diffraction. The x-ray measurements require calibration. An SRM of quartz powder in the respirable dust size range is to be produced in cooperation with NIOSH and OSRM. Dr. R. McKenzie (553--Gas and Particulate Science) will certify that the material is within the "respirable" range. Following that, we will determine the percent of amorphous silica (see above), relative intensities, and reference intensity ratio.

Standard Reference Materials--Crystallite Size. (A. L. Dragoo, C. R. Hubbard) The goal of this project is to develop methods for certification of a series of crystallite size standards. Three methods are being studied as means for the

preparation of submicron size MgO crystallites: (1) generation of MgO smokes by burning Mg metal, (2) precipitation of a Mg compound followed by its decomposition to the oxide, and (3) micromilling of crushed single crystal MgO. Filtration and sedimentation are being used to fractionate the milled powders with respect to particle size. SEM and image analysis will be used to measure the dimensions of the particles. A test sample prepared by the precipitation method is being used to evaluate our implementation of the Warren-Averbach procedure for determination of mean crystallite size and residual strain. Advice from Prof. J. Cohen (Northwestern University) and Dr. J. I. Langford (University of Birmingham) has been used in development of our procedures for data analysis. Ms. J. Whang, a summer student from MIT, is implementing the algorithm as well as plotting options. Dependent on results on crystal habit we may also attempt to determine the distribution of crystallite size. For meaningful results, the distribution of column lengths within one crystallite must be very narrow so that the derived distribution represents the distribution of crystallite sizes. The profile models described above will be tested to see if they can be used to help resolve the line overlap problem.

Standard Patterns. Seven Research Associates of the JCPDS--International Centre for Diffraction Data (M. C. Morris, Director; H. F. McMurdie, Consultant; E. H. Evans; B. Paretzkin; N. Panagiotopoulos; Harry Parker; and C. Wingo) continue to produce high quality x-ray diffraction patterns as well as to evaluate and edit data from the literature. Section 18 of NBS Monograph 25 was published in September 1981. This is the 27th of the series of "Standard X-ray Diffraction Patterns." Section 18 will include approximately 60 experimental patterns as well as a review of methods used at NBS for obtaining the patterns.

Each year the JCPDS publishes a supplement to the powder data file (PDF). The complete file, recognized as the standard reference source for powder diffraction analysis, consists of 30 sets of data from nearly 35,000 crystalline phases. Due to the continuous growth of the PDF, a major effort of the JCPDS is to produce subfiles for selected fields. Subfiles currently available are: (1) Frequently Encountered Phases/Common Phases (FEP/CP), (2) Minerals, (3) Metals and Alloys, and (4) NBS Patterns. M. C. Morris, Chairperson of the FEP/CP subcommittee continues to review and improve that subfile. Under her direction, the Associateship is adding new patterns to the PDF and replacing poor patterns with high quality data. Approximately 90 percent of the patterns, both organic and inorganic, to be published in Section 18 of the Monograph, have been designated for the FEP/CP subfile. For FY82, the group expects to submit approximately the same percentage. The remaining 10 percent of the patterns are of less common phases of minerals, alloys, ceramics, or forensic materials for which samples were available and for which the pattern was absent or not well represented in the file.

The Associateship also continues to work on methods and procedures that are useful to the diffraction community. For instance, a considerable amount of time is being spent on finding means of obtaining reliable intensities. During FY80, the group began reporting a reproducibility factor for the measurement of relative intensities. This factor enables a user of the data to evaluate the accuracy of the intensity data. Also, in accordance with the recommendation from the American Crystallographic Association, the Associateship now includes in its publication a figure of merit (FM). This FM enables one to assess the

quality of the experimental spacing measurements. In FY82, we will be using the spray-drier to reduce time and improve data quality for relative intensity measurements. We also plan to measure a majority of the patterns with the automated system.

JCPDS Activities. S. Block, C. R. Hubbard, J. K. Stalick, and A. D. Mighell continue to be involved in activities of the JCPDS-International Center for Diffraction Data. Of particular importance is the JCPDS-NBS program on standard patterns (discussed above).

The Data Base Subcommittee (including C. R. Hubbard, Chairman, J. K. Stalick, and A. D. Mighell) has seen major progress by the JCPDS in adopting the NBS*AIDS80 data base format and program (see Crystal Data Section) as well as the HP2645 formatting terminal for data entry. NBS*AIDS80 is a computer program for crystallographic data evaluation used by Crystal Data and the JCPDS Research Associateship. One operation mode of this program is to write a data base entry. The data base format for the JCPDS and Crystal Data is identical in order to facilitate future exchanges of data between centers. The formatting terminal is a data entry station for rapid and accurate keyboarding compatible with the requirements of NBS*AIDS80. Currently, the JCPDS plans to convert their entire operation to use of a computer data base within five years. As a test of the feasibility of this project, two complete sets of PDF data were processed through NBS*AIDS80. First, the output for the 2000 patterns in Set 23 was given to ten JCPDS members for review. Their responses led to significant debugging and addition of enhancements of NBS*AIDS80. A test for systematic errors, independent of what form, was derived based on a publication by Young (Ann. of Math. Stat., Vol. XII, No. 3, p. 293). Coupled with other evaluations this test provides a sensitive indication of non-random variability. Finally, data from Set 24 were processed and are being reviewed by JCPDS editors and staff. The output of both sets will be used to revise the PDF cards for these two sets, which will be published in book form.

The Methods and Practices Subcommittee (C. R. Hubbard, member) is working toward publishing a set of test problems for x-ray powder diffraction least-squares programs. To be included with the lattice constants are the calculated figures of merit, M(20), F(N) and our non-random variability test values. Data from the NBS Monograph Series are being used for the test data.

The Education Subcommittee (C. R. Hubbard, member) has finally seen its workshop handout on PDF Search/Match methods published. This handout, which was first used at the Albany X-ray Clinic (June, 1981), was used at the International Union of Crystallographers' meeting and the Denver X-ray Conference in August. Work is continuing (C. R. Hubbard with seven JCPDS members) on an ACS Audio course describing use of the PDF as well.

Other activities include Crystal Data Subcommittee (A. D. Mighell), the Long Range Planning Committee (C. R. Hubbard), and the Board of Directors (C. R. Hubbard).

High Intensity X-ray Sources for Microdiffraction
Subtask 2 of Task 12153

F. A. Mauer

Microdiffraction methods are frequently needed to identify minute inclusions or reaction products and to obtain diffraction data from samples confined in environmental chambers such as the diamond anvil pressure cell. A long-standing problem is the low intensity of diffraction patterns obtained from samples that are often more than three orders of magnitude smaller than those used with a conventional powder diffractometer. Two approaches to obtaining improved intensities have been tried: a 12 kW rotating anode generator and a synchrotron source.

Rotating Anode. A rotating anode generator purchased in cooperation with Division 564 has been used to increase both the count rate and resolution of energy dispersive powder diffraction data obtained with the diamond anvil pressure cell.

Although the x-ray output is from ten to fifteen times greater than that of the sealed tube generator (depending on choice of target and focal spot size), this does not necessarily translate into an increase in intensity of the same magnitude. A decision was made to trade off part of the intensity to obtain improved resolution. The sample-to-source distance was increased from 5.73 in. to 14 in. This change reduced the useful x-ray flux by a factor of six, but decreased the divergence of the incident beam by a factor of 2.4. At the same time, a new receiving slit was made to match the radius of curvature of the cone of diffracted radiation at $2\theta = 14°$. (The slit can be optimized in this way because the energy dispersive method uses a fixed diffraction angle.) The net effect of these changes has been a 40 percent increase in counting rate and a 33 percent reduction in the width of diffraction peaks. A diffraction pattern suitable for measuring lattice parameters can be obtained in 5 h, even with an extremely light scatterer such as ice VII. The improved resolution has eliminated some of the uncertainty about the semiconductor-conductor transition of GaAs at 18 GPa. This transformation was under consideration by an international committee for a marker on the fixed point pressure scale. The transition is quite sluggish, extending over a 0.8 GPa range. It was thought for a time (on the basis of low-resolution data obtained from the sealed tube generator) that a second transformation might be involved. However, data obtained on the rotating anode unit show the same triplet of lines in the range from 20 to 22 keV at all pressures above 18.0 GPa indicating that a single, sluggish transformation occurs (see below).

Synchrotron. Although the rotating anode can provide a marginal increase in x-ray intensity in the home laboratory setting, utilization of one of the synchrotron sources can provide a really dramatic increase. Energy dispersive diffraction measurements with the diamond anvil pressure cell represent a nearly ideal application for synchrotron radiation, and work has been in progress at major synchrotron sources since 1976. Scientists at NBS and from the Naval Research Laboratory have formed a "Participating Research Team (PRT)" for the development of two beam lines at the National Synchrotron Light Source under construction at Brookhaven National Laboratory. Synchrotron radiation will be available on a regular basis soon after January 1982.

Meanwhile, we have made use of the excellent facilities available at the Cornell High Energy Synchrontron Source (CHESS) for a preliminary experiment.

A new method of obtaining x-ray powder diffraction data from samples in the diamond anvil pressure cell was tested at CHESS during the week of May 4-9 by F. A. Mauer and R. G. Munro in collaboration with B. W. Batterman, D. Mills, and Donald H. Bilderback of Cornell University. Professor I. Fujishiro (guest worker from Nagoya University) joined the team for the final three days. The new method retains the fixed angle feature of the energy dispersive method which makes it so adaptable to environmental chambers such as the high pressure cell. In order to achieve improved resolution, it substitutes wavelength scanning of the incident radiation for spectral analysis of the diffracted beam. Since the energy resolution of the channel-cut silicon monochromator on the C2 line at CHESS is far superior to that of any solid state detector system ($\sim$ 10 eV vs 200 eV FWHM @ 20 keV) it should be possible to obtain a substantial improvement in resolution if the divergence of the slit system can be kept below about 10^{-3} radians.

The wavelength scanning microdiffractometer designed and built at NBS makes use of a detector with an annular receiving slit that intercepts the entire cone of radiation diffracted at a fixed angle of $2\theta = 12^{\circ}$. This feature increases the efficiency by a factor of 20 compared to a conventional powder diffractometer and is of great importance because of the severely restricted volume of samples in the high pressure cell ($< 2 \times 10^{-6}$ cm^3). Use of the complete cone of diffracted radiation also tends to alleviate another problem encountered in microdiffraction techniques. It can be shown that in the case of the diamond cell the number of crystallites contributing to the diffracted intensity is often fewer than ten. This number is too small to effectively average out variations in the size of individual crystallites, and serious fluctuations in intensity are likely to occur. Utilization of the full cone results in a 20-fold increase in the number of crystallites that contribute at each point on the diffraction profile. The effect of graininess or preferential orientation is greatly reduced.

Powder patterns are obtained by recording the total output of the detector while scanning through a range of wavelengths with the incident beam monochromator. A peak is observed whenever the wavelength of the incident beam is related to one of the characteristic d-spacings of the sample according to the Bragg equation $n\lambda = 2d \sin \theta$ or, in terms of energy $E = (6.19905/\sin \theta) \cdot 1/d$, where θ is a constant.

The existing Rigaku detector used for the CHESS experiment has an annular slit 30 mm in diameter and 0.2 mm wide. At $2\theta = 12^{\circ}$ the divergence of the slit system ($\Delta\theta = 2.3 \times 10^{-3}$ radians) is so great that no improvement in resolution can be expected. Nevertheless, data obtained with this unit will be more useful for estimating the counting rates than can be expected from a system with higher resolution.

Patterns were obtained at CHESS on five samples, two of which were in diamond anvil cells. A step size of 40 eV was used so that each step would correspond to the energy increment between channels for our solid state detector system. The pattern for CdS in the diamond cell recorded at CHESS in approximately 8 min is shown in figure 2 along with the pattern obtained in 3 h with the rotating anode unit.

The following conclusions are based on the results obtained at CHESS:

1. The count rate for each 40 eV increment of energy is greater by a factor of 10^4 than it is for the same increment using the rotating anode source.

2. The full width of the diffraction profile at 20 keV is 460 eV as predicted from the divergence of the slit system. This will be reduced to ~ 100 eV for our next test.

3. Graininess is a severe problem for samples with an average crystallite size of 10 μm. Samples with particles in the 1 μm range give smooth diffraction profiles.

4. The probability of encountering single crystal spots from the diamonds is increased because of the use of the complete cone of diffraction. These reflections, which are more intense by two or three orders of magnitude than powder diffraction lines, can be eliminated by selecting diamonds having the 110 direction perpendicular to the beam direction.

5. Specimen fluorescence, as in the case of the CdS sample, is much less of a problem than it is with the solid state detector system (see figure 2). While one is scanning the region from 22.5 to 26.5 keV where interference would occur, the energy of the incident beam is below that of the K absorption edge at 26.7 keV, and no fluorescence occurs.

Based on the results obtained at CHESS, it seems clear that we can reduce the divergence of our slit system by a factor of five without sacrificing peak counting rate. To do this, we will need to build a larger detector using a five inch crystal (available commercially). Our calculation indicates that a resolution of 0.5 percent can then be expected, which provides a substantial improvement over the 1 percent resolution of existing microdiffractometer or energy dispersive systems. We will lose a factor of about 500 in speed because points on the diffraction profile must be recorded sequentially. The time required to record a high resolution pattern will still be under two hours.

Future research plans involving synchrotron radiation include the determination of partial structure factors for amorphous materials containing anomalous scatterers. The recently proposed frequency modulated x-ray diffraction technique is to be tested. If the expected orders-of-magnitude improvement in sensitivity is realized, the method will be particularly suitable for radial distribution studies with the diamond anvil cell (see below under High Pressure Research).

Characterization of Power Plant Fuels and Ash
Subtask 3 of Task 12153

C. R. Robbins

A program to study power plant fuels and ash, sponsored by the NBS Office of Recycled Materials, was initiated in May 1979. The study involves development of quantitative methods of phase analysis by x-ray powder diffractometry, and will be complemented by several other instrumental methods of chemical analysis. The work will produce a body of information on the behavior of a broad spectrum

of fuel feedstocks, burned in a variety of plants under known operating conditions. This systems approach, which has not been explored before, will provide data needed for ash management techniques and for a better understanding of leaching mechanisms. It could lead to improvements in precipitator designs, and to better utilization of coal by-products.

Resources of this project have initially been directed toward the selection and development of techniques for characterization, with emphasis on the development of quantitative x-ray powder diffractometry methods. A collaborative effort between Professor R. L. Snyder of Alfred University and Dr. C. R. Hubbard of this group in modifying existing software in order to utilize new, automated NBS x-ray equipment is completed (see above). A spray-drier for x-ray sample preparation has been constructed in the NBS shops and is now operational.

A method of preparing powder specimens for SEM and x-ray fluorescence analysis was devised by Dr. A. L. Dragoo. The method involves embedding the particles in an epoxy and then sectioning and polishing the resulting specimen. Dr. Dragoo used this technique in a study of the morphology and related chemistry of NBS SRM 1633a Coal Fly Ash. Collaborative work with Dr. L. P. Cook of NBS was initiated in July 1981 and will include study of the fuel residues by SEM, TEM, and STEM.

A collaborative effort with Dr. C. Powell and Dr. N. Erickson of the NBS Surface Science Division was also initiated in July 1981 to study the surface chemistry of the finer ash fractions by Auger and SIMS methods, both before and after leaching.

Along with the ORM project, a new program under the sponsorship of the Department of Energy, and the technical management of the Laramie Energy Technology Center was established at NBS in May 1980. The program involves several groups at NBS, and one of its objectives is to establish the behavior of fossil fuel wastes subjected to a variety of leaching procedures. The program will involve interaction with the Analytical Chemistry Division. The Ceramics, Glass, and Solid State Science Division is responsible for the physical and chemical characterization of the specimens, both before and after leaching. Receipt of samples for analysis has been delayed. In the interim, three samples of chemically analyzed coal fly ash have been obtained and leached by two different methods. These specimens will serve as reference standards for our analytical procedures. One of these samples (NBS SRM #1633a Coal Fly Ash) has been studied in some detail by XRD, SEM, and light microscopy.

Particle size distribution has been measured by six different methods and results are being compared. Preliminary qualitative x-ray data on 1633a suggest that differences between leached and unleached specimens may be detected by x-ray diffraction.

Sixty specimens of ash from refuse derived fuels (RDF) and from coals have been received from the Chemical Thermodynamics Division for x-ray analysis. This is a cooperative effort, intended to complement their calorimetric work on alternate fuels, and to contribute to the formulation of ASTM test procedures for these new materials. The samples were heated in air at temperatures up to 1075 °C. Qualitative x-ray analysis suggests which chemical reactions may be

taking place at the various ashing temperatures. The phase assemblages for the RDF ash samples are remarkably similar over the entire range of temperatures studied. A joint publication on this work is in preparation.

Several suites of carefully selected and documented samples have been received from interested groups for analysis. All samples received have been characterized by preliminary qualitative methods. Among these samples, ash from the burning of a blend of coal and RDF is of considerable interest and will be studied in detail.

Characterization of Prehistoric Ceramics. Some additional work is in progress with Dr. V. P. Steponaitis (Anthropology Department, SUNY at Binghamton) to complete a joint publication on prehistoric pottery from Moundville, Alabama, a site occupied between A.D. 900 and A.D. 1600 by Indian tribes. Phase analysis by optical microscopy and by x-ray diffractometry has identified the raw materials used, and the range of firing temperatures reached in making the pottery.

High Temperature Applications of Structural Ceramics
Subtask 4 of Task 12153

A. L. Dragoo. R. G. Munro

This research in collaboration with Division 562 is part of a Center-wide program sponsored by DOE's Advanced Research and Technology (ART) Fossil Energy Materials Program. The objective of this work is to improve understanding of high temperature microstructural and mechanical behavior of structural ceramics that have potential use in heat engines and heat recovery systems. One goal is to measure the oxidation rates of SiC ceramics and to develop an understanding of the role of oxidation in the degradation of strength of these ceramics under performance conditions. To attain this goal we are engaged in the following activities: (1) a literature survey to establish knowledge, data, and problems regarding oxidation kinetics and mechanisms for SiC and to obtain physical quantities and theories for the calculation of oxidation-produced strain in SiC; (2) XRD measurement of the rate of formation of oxide phases and measurement of overall oxidation kinetics by weight gain or by rate of oxide layer growth; and (3) SEM study of microstructure changes brought about by oxidation.

Studies of the oxidation of pyrolytic β-SiC in CO-CO_2 mixtures found β-crystobalite to be the principal oxidation product. Preliminary XRD studies of commercial SiC samples indicated that tridymite was the predominant phase to form in the reaction layer at temperatures between 1200 and 1400 °C, whereas at 1500 °C a significant amount of a glassy phase appeared to form.

A high temperature furnace for in situ XRD studies is being developed. This furnace is a modification of an earlier furnace developed by F. A. Mauer and L. H. Bolz. The concept for the present furnace differs radically from the earlier design in the use of the specimen as its own heating element rather than in the use of an external heating coil. It is anticipated that by this new concept improved temperature uniformity and temperature up to 1500 °C can be realized.

Chemical Bonds In Ionic and Partially Ionic Compounds. For many years short-range interactions in crystals have been represented principally by a Born-Mayer repulsive potential plus one or two van der Waals terms for the attractive potential. These central-force potentials have been restricted to pairs of near neighbor (NN) and next-nearest neighbor (NNN) atoms. A variety of potentials also have been introduced to model noncentral-force interactions, such as those arising from covalent bonds, and to model many-body interactions.

As part of this work, a bond-deformation formalism was developed which describes the interactions in the entire complex of NN atoms about a fiducial atom. This formalism includes both central-force and noncentral-force type coupling constants and can serve as a framework in which model potentials can be tested and compared. Analysis of the force constants in terms of the symmetry of the crystal establishes fundamental relationships between the force constants.

The coupling constants for NN bond deformations and some NNN bond deformations were identified for the case of crystals having the rocksalt structure--the alkali halides and the alkaline earth oxides. For NN bonds there is a single, non-zero first-order bond-stretching contant; there are three second-order bond-stretching constants, one of which involves one bond, and two of which involve two bonds; there are five bond-bending constants, one of which involves one bond angle and four of which involve two bond angles; and there are three stretch-bending constants which involve the stretching of a bond and the bending of a bond angle. An equilibrium condition relates the first-order constant to the second-order constants. The bond-stretching constants for NNN bonds can be shown to be reducible to linear combinations of the coupling constants for NN bonds; this is a consequence of the law of cosines.

Expressions were derived for the elastic constants in terms of these coupling constants, for the force constant for optic mode displacements and for the "Cauchy discrepancy," defined as a $(C_{12} - C_{44})$, where "a" is the NN bondlength and C_{12}, C_{44} are elastic constants. The NN and NNN central-force contributions to the coupling constants were determined. A further empirical relationship is sought between some of the noncentral coupling constants.

A paper currently is in progress on the formalism and its application to rocksalt structure crystals. The model will be extended to other crystal structures which include materials for which noncentral forces play a significant role in the material properties.

High Pressure Studies
Subtask 5 of Task 12153

S. Block, G. J. Piermarini, R. G. Munro

Cadmium Sulfide. In cooperation with Watervliet Arsenal, we have studied the preparation, characterization, and various physical properties of CdS as a function of pressure. Watervliet Arsenal had discovered that one particular sample of CdS from one particular supplier gave anomalous magnetic properties when pressure quenched from about 4 GPa - 1 GPa above the semiconductor-conductor transition. The magnetic properties indicated that this material could be a "high temperature" superconductor. Chemical analysis by the Analytical Chemistry

Division indicated that the active sample contained chloride ions. Chemical synthesis by both solid state reaction and precipitation from solution was initiated at NBS. We were able to produce a sample prepared by the precipitation technique which produced the magnetic anomaly in the pressure quenched material. Chemical analysis of the material prepared by preciptation indicated that the chloride ion content of the CdS is a function of the normality of the $CdCl_2$ solution from which the sulfide is precipitated by H_2S. Furthermore, the chloride is of two forms, one which is loosely bound and removable by solution and another portion which is retained probably within the lattice. High pressure studies of the microscopic, electrical, and structural properties of highly doped (chloride) cadmium sulfide were undertaken. Preliminary results indicate that the chloride concentration drastically affected all of the above properties. Pure CdS transformed at 2.25 ± 0.05 GPa. The transformation was accompanied by (a) an electrical resistance change of approximately four orders of magnitude, (b) opacity, (c) a structural change from the Wurtzite to the NaCl structure, and (d) a return to the Wurtzite phase upon release of pressure. Chloride "doping" changed all the properties drastically. At the highest level (6.3 percent Cl) the electrical resistance remained high, the color remained orange but the structure changed to the NaCl form at approximately 4.8 GPa. Lesser amounts of chloride ion also changed the transition pressure but not as drastically, and the retained phase after quenching always contained the NaCl form. The NaCl phase was not photoconductive. The pressure at which the phase transformation occurred was also sensitive to hydrostatic effects being lowered by nonhydrostatic environments. The pure material transformed at 2.9 GPa when determined optically in a hydrostatic fluid. The compressibility of CdS was also measured by x-ray diffraction. The volume of the pure material changed by -3.8 percent to the transition pressure and by an additional -17.7 percent at the transition.

Pressure Dependence of Viscosity, Hydrostatic Limits and Glass Transition Pressures of Liquids. A hydrostatic environment is essential for the accurate characterization of high pressure measurements. It is now well documented that significant differences in the results of high pressure measurements can occur, and these subsequently can lead to appreciable error in the interpretation of the results. Hence, an ever-increasing demand exists for well characterized hydrostatic environments at very high pressures.

Advances in measurement technology for characterizing hydrostaticity were developed at NBS and are presently being employed to explore and extend the hydrostatic range accessible to experimentation. The technology includes the measurement of the viscosity of liquids as a function of pressure. Such viscosity data can be used to estimate the amount of time required for the relaxation of unwanted transient shear stresses generated in a liquid as a result of a change in pressure. Additional information concerning the pressure at which the liquid becomes a glass (glass transition pressure, P_g) can be obtained readily from ruby fluorescence line-broadening measurements.

Utilizing the critical point model for high pressure viscosity as proposed by us, the two pieces of information, (1) pressure dependence of viscosity and (2) glass transition pressure, can be used to characterize the pressure transmitting medium in terms of absolute viscosity, glass transition pressure, and rate at which the glass transition is approached.

The pressure dependence of the viscosities and the glass transition pressures (hydrostatic limits) for the binary methanol-water and ternary methanol-ethanol-water systems have been measured for several compositions. The diamond anvil falling sphere viscometer was employed in conjunction with the ruby fluorescence pressure measurement and line-broadening methods. The work was done in collaboration with Prof. I. Fujishiro from the University of Nagoya, Nagoya, Japan, who was on a nine-month stay at NBS (September 1980-May 1981) to learn about diamond cell techniques and their possible application to the area of tribology of lubricants. Professor Fujishiro was entirely supported by the Japanese Ministry of Education while at NBS.

The binary and ternary systems were selected for study for several reasons:

1. Mixtures of these liquids have low freezing point eutectic compositions which have a tendency to exhibit high freezing pressures.

2. Mixtures of these liquids tend to superpress rather than crystallize which permits the glass state to be achieved through a steady increase in viscosity with increase in pressure.

3. Superpressed mixtures of these liquids tend to have high glass transition pressures, P_g, and therefore, a large hydrostatic range, e.g., methanol: ethanol, 4:1 by vol, has a P_g of 10.4 GPa.

4. The probability of extending the hydrostatic limit above 10.4 GPa through a detailed study of these systems is high.

As a result of this work several new hydrostatic pressure transmitting media were discovered which exceed the previous limit of 10.4 GPa. The best medium is a ternary mixture of methanol:ethanol:water whose composition is 16:3:1 by volume. Its hydrostatic limit of 14.5 GPa at room temperature gives an increase of about 40 percent over the previous medium. Viscosity data were obtained on several liquid mixtures and permitted extrapolations to be made to the glass transition pressure based on a critical point model for viscosity developed at NBS. The data for 19:1 methanol:water were used to examine the extent to which the high pressure viscosity model, $\eta = A(1-P/P_g)^{-\nu}$, can be used for extrapolation. The procedure was to use only a portion of the data and to compare the resulting extrapolation to the remaining data. In each case, the value of the glass transition pressure, 12.1 GPa, was taken from the ruby line broadening study. The results are shown in figures 3 through 5.

In the first figure, only the data from 3.6 GPa to 4.3 GPa were used. The extrapolation was found to be good to about 5.1 GPa. In the second figure, data to 5.0 GPa were used, and the extrapolation was excellent to 7.2 GPa, the highest pressure observed.

While the foregoing establishes the plausibility of extrapolating on the basis of the critical point model, further consideration must be given for extrapolations to pressures near the glass transition. The model treats the glass transition as a singularity; i.e., the model tends to infinity as P_g is approached. However, the actual value of the viscosity at the onset of the glassy state is by convention, 10^{13} poise. To estimate the reliable range of

extrapolation beyond 7.2 GPa, two tangent lines to the model curve were found as follows. A lower limit for the viscosity can be obtained by drawing the tangent line at 7.2 GPa. An upper limit occurs at that pressure for which the tangent line, when extended to the glass transition pressure, passes through the value of 10^{13} poise. In the third figure, a value of 2 x 10^{13} poise was used to allow for the least squares uncertainty. The correct viscosity curve should come between these tangent lines. As shown in the third figure, this procedure indicates that the model extrapolation should be good to about 8 GPa. Note also that the tangent lines provide a secondary estimate of the viscosity to 12.1 GPa.

It is possible that the utility of the model can be extended in two ways. First, by shifting the singularity of the model to a pressure greater than Pg, assuming a well defined criterion, the useful range of extrapolation could be increased, possibly to the glass transition. Second, by applying a self-consistency requirement, it might be possible to predict the temperature dependence of viscosity. The only additional experimental information required is temperature dependence of P_g, which can be determined in our laboratory.

Raman and X-ray Investigations of Ice VII. Measurements of the pressure dependence of the lattice parameter of Ice VII were made by the energy dispersive powder diffraction method utilizing a diamond anvil pressure cell. The ruby fluorescence method was used to measure the pressure. Ice VII was studied at room temperature to 36.0 GPa. Generally the lattice parameter at each pressure was based on the (110), (200), and (211) reflections. The largest portion of the error is due to the uncertainty of the pressure in the highest ranges, arising from the nonhydrostatic character of Ice VII. For example, in one instance of nonhydrostatic stress, the pressure measured by the ruby fluorescence method in a sample approximately 0.2 mm in diameter by 0.1 mm thick, ranged from 23.7 GPa to 26.2 GPa. The lattice parameter of Ice VII decreased monotonically from a = 3.367 ± 0.004A at 2.30 GPa to a = 2.896 ± 0.007A at 36.0 GPa. This leads to an O-O distance change from 2.916A to 2.508A. There was no indication of a phase transition over this pressure range.

In collaboration with Prof. G. Walrafen of Howard University, Raman spectra of Ice VII were obtained to 30.0 GPa at room temperature. Both x-ray nearest-neighbor O-O distances (r_{OO}) and Raman OH-stretching peak frequencies ($\Delta\nu$ in cm^{-1}) were observed to decrease at a decreasing rate with pressure rise. Although $\Delta\nu$ values were found to be roughly linear with r_{OO} between 2.5 and 2.9A, more refined analysis revealed a cubic dependence resulting, upon extrapolation, in a minimum at $r_{OO} \sim 2.35$ Å. This minimum suggests that a symmetric hydrogen bond, O-H-O, and thus a new structure, may be attained at very high pressures, roughly 50 to 75 GPa or above. The decrease in $\Delta\nu$ observed with pressure rise is thought to reflect an increase in the OH distance (r_{OH}) with decreasing r_{OO}, for r_{OO} values > 2.4 Å. Treatment of O-H···O oscillators, using assumptions in agreement with observation, predicts that $\Delta\nu \sim a/r_{OH}^2$ between 2.5 and 2.9 Å. This prediction was confirmed when values of $(2943\ cm^{-1}/\Delta\nu)^{\frac{1}{2}}$ for various r_{OO} values, were found to agree quantitatively with a plot or r_{OH} versus r_{OO} obtained from published neutron and x-ray diffraction data for other systems.

The OH stretching frequency progressively gets weaker in intensity and shifts toward the diamond fluorescence region with increasing pressure, and at 30 GPa the intensity is too weak and obscured to be measured. To avoid this problem D_2O, whose stretching frequency is far from the diamond fluorescence, will be studied to higher pressures. X-ray measurements have been completed to 34.0 GPa and specially selected diamond anvils with low fluorescence properties have been obtained and are presently being assembled for the Raman work.

Equations of State. A computer program has been developed which interprets compression data in terms of several representations of the isothermal equation of state. Included are the Birch, Birch-Murnagham, Murnagham, Bardeen, Born-Mie, Bridgmen, Tait, and Olinger-Halleck equations and the low pressure series limit. Further programming which applies regression analysis to the compression data to evaluate the isothermal bulk modulus has been completed also.

These programs have been used in the study of H_2O VII and D_2O VII. The first figure shows the fit of the Tait equation to the H_2O VII data, and the second figure shows the bulk moduli of both H_2O VII and D_2O VII as determined by the regression analysis and by the Tait equation. It appears that D_2O VII is somewhat more compressible than H_2O VII at high pressures, with the pressure at which the bulk moduli are equal being about 16 GPa. The differences, however, have magnitudes that are about the same as the uncertainty in the results, and further studies are being made.

Radial Distribution Studies. The structure of an amorphous material can be described in terms of its radial distribution function (RDF) and its Fourier transform, the reduced structure function. Previously, studies were made on data analysis procedures appropriate for the extreme conditions of high pressure experiments. Now the adaptation of those results to the diamond anvil pressure cell are in progress. The material being studied is an amorphous metal of iron and tungsten.

The procedure being followed can be broken into several steps. The first step, which has been completed, is the determination of the RDF for a sample not in the pressure cell and using high resolution angle dispersive diffractometry. In this experiment, the data reduction techniques are easier than for the energy dispersive method, and a larger range of data can be acquired. This establishes a reference RDF for comparison with later stages of the development. Figure 8 shows the differential RDF that results from the angle dispersive data. It may be noted, for example, that the first peak occurs at about 2.7 angstroms. The atomic radius of tungsten is about 1.37 angstroms which suggests a tungsten-tungsten distance of 2.74 angstroms. The corresponding values for Fe-Fe and Fe-W distances are 2.52 and 2.63 angstroms. The concurrence of the W-W distance with the location of the first peak in the RDF indicates that the x-ray scattering is dominated by the tungsten component of the sample, as might be expected on the basis of the atomic scattering factors of the two elements.

The second step of the procedure is a repetition of the first one except that the energy dispersive method is used for the data. The most significant additional complications are due to the more restricted data, the required absorption correction as a function of x-ray energy, and the required incident beam profile. This stage is nearing completion with only a numerical refinement yet to be made to treat overlapping peaks more accurately.

The third and last step is to examine the sample in the pressure cell. In this case, the absorption and scattering effects of the diamond windows and of the pressure transmitting medium must be treated. These effects are not expected to present any real difficulties since the expected data limitations are already incorporated in step two.

Gallium Arsenide: Compression to 31.0 GPa, Structural Transformation, Transition Pressure and Use as a "Fixed Point": The International Union of Crystallography's Commission on Crystallographic Studies at Controlled Pressures and Temperatures has conducted round-robin studies of the reproducibility of high pressure transformations in semiconductor materials. These materials exhibit pressure induced semiconductor-conductor type transitions which are accompanied by large changes (5 to 6 orders in magnitude) in resistivity as well as a structural change. The transitions usually can be detected by several means including x-ray diffraction and optical and electrical methods. These features make the semiconductors prime candidates for markers on the "Fixed Point" Pressure Scale. The previous material evaluated by the Commission was ZnS which has a transition in the region of 15.0 GPa. The ZnS round-robin was conducted by S. Block as Chairman of the Commission. The encouraging results of that study have moved the Commission to conduct another round-robin. GaAs, which has a transformation reported to be in the vicinity of 18.0 GPa was chosen in order to provide a well characterized fixed point in the pressure regime above 15.0 GPa where there is a serious need for improved agreement in the various calibration techniques. The Commission's round-robin activities in the U.S. were conducted by G. J. Piermarini who provided well characterized GaAs single crystal samples (from S. Akimoto, University of Tokyo) to six laboratories in the U.S. including NBS. These laboratories were selected to provide a variety of pressure generating systems, calibration methods and environments.

At NBS the newly developed energy dispersion method was used in conjunction with a diamond anvil pressure cell to obtain x-ray powder diffraction data on GaAs to 31.0 GPa. Measurements were made using a rotating anode generator as well as a conventional x-ray source. The ruby fluorescence shift was used to measure the pressure. Calibration was based on the linear shift given by the Decker Equation of State for NaCl. The results are shown in figure 9 in the form of a compression curve for GaAs. The normal cubic phase was found to transform to an orthorhombic phase in the vicinity of 18.0 GPa. The transformation, which was accompanied by a 13 percent decrease in volume, was found to be very sluggish and to occur over a rather large pressure range, 0.8 GPa. The appearance of the material itself changes at the transition from red, translucent to opaque (out to a wavelength of 1100 nm). This change is indicative of a transformation to a conducting state. Because the transformation in GaAs cannot be well characterized, it is unsuitable for use as a marker on the Fixed Point Scale. This conclusion is in agreement with other reporting laboratories. The current chairman of the Commission, S. Akimoto, will report on the results of the round-robin study at the 12th International Union of Crystallography Meeting to be held August 16-25, 1981, in Ottawa, Canada.

Nuclear Waste Management
Subtask 6 of Task 12153

R. G. Munro

In the subtask "Leachability Mechanisms: Concepts and Theory," attention is being given to the construction of a comprehensive mathematical model for leach test measurements. Primary consideration is being given to the experimental conditions of the MCC 1 measurement which involves the use of a monolithic sample of known surface area which is held statically immersed in a leachant having a fixed volume such that the ratio of sample surface area to solution volume is 0.01 mm^{-1}. The waste substance is assumed to be enclosed in a solid host that is suspended in a liquid solvent, and the entire system has a closed finite volume. Both the waste substance and the solid host can be allowed to react chemically with the solvent, and the reactants can be allowed to diffuse, precipitate, or adhere to the host-solvent interface.

As an example, consider the formation of a reactant (in the solution) that subsequently adheres to the solid-liquid interface. It can happen that this layer flakes from the interface when the deposited mass reaches a critical value, and this behavior must affect the interpretation of the observable data. Leaching mechanisms, in particular, are often deduced, or guessed, on the basis of the time dependence of Q, the amount of the substance that has been leached. Leaching controlled by simple diffusion should have Q proportional to the square root of the elapsed time, t. Leaching controlled by the dissolution of the host matrix should have Q proportional to t. Hence, by examining Q vs t, the dominant mechanism could be deduced if there were only these two cases to consider.

However, if the leachant reacts with the solvent and forms an adhered layer of reactant on the solid-solvent interface, then the Q vs t plot is not so simply interpreted. It has been hypothesized that the flaking of such a layer would produce a linear t-dependence. By the above criteria, this would imply a mechanism that was not actually operative.

A detailed examination of the chemical-reaction-deposited layer-flaking problem has been performed numerically with results that are illustrated in figure 10. The diffusion and reaction parameters were chosen to exaggerate the effect of flaking in the interval of 300 computer time steps.

Three possible interpretations are evident in the case of flaking: (1) over only short times, there is a parabolic rate, (2) over only long times, there is a linear-like rate, and (3) over all times, allowing only discrete points as in an experiment, a second parabolic rate possibly could be produced.

These observations emphasize the need to examine the chemical details of the solid-solvent interface if reliable leach test measurements are to be made.

Data Centers for Materials and Components for Fossil Energy Applications
Subtask 7 of Task 12153

H. M. Ondik, A. Perloff, with B. W. Christ (562)

The Fossil Energy Materials and Components Data System consists of two Data Centers operating cooperatively to provide a central data base of materials and

components performance and properties data. One element of the system is the Materials Properties Data Center which is responsible for compiling information on construction materials for coal conversion use and includes data for MHD power generation as time allows. This Center is now staffed by personnel from the Ceramics, Glass, and Solid State Science Division (Ondik and Perloff). The major source of the data is the Data Center's library of DOE materials research contractors' reports. There are about 50 DOE-funded projects generating materials properties and performance data for coal conversion and utilization. About a dozen of these projects have generated MHD materials data. As time allows, other information sources are sought to expand the data base. Computer storage of the materials properties data base and access to it is handled by a commercial data base management system. In time, non-NBS users will have direct on-line access to search the system.

The other segment of the information system is the Materials and Components Plant Performance Data Center now staffed by B. W. Christ of the Fracture and Deformation Division (562). The source of the information consists of reports of materials and component failures submitted to DOE on a voluntary basis by the various coal conversion plants. The information is abstracted and entered into computer storage under a system allowing high speed retrieval with a variety of search schemes. One goal of the Center is to develop the file and correlate operating experience so that trends will be observed indicating primary causes of plant failures for the guidance of designers and operators of coal conversion plants.

All of the data from both Centers are now under the control of one Data Base Management System (DBMS) for storage and retrieval. The nature and structure of the data sets of the two Centers are too different to permit storage in one file, but the same DBMS can be utilized to handle several files.

The existing computer file of the Materials and Components Plant Performance Data Base contains some 500 reported failures. Although fewer pilot plants are now operating, resulting in a slow rate of increase of the data file, there is continuing interest on the part of the user community. Since the data base was started in 1976, hundreds of requests have been answered by distributing over 17,000 computer abstracts and over 800 complete copies of operating event or failure reports. The Center has also given out some 40 copies of reports consisting of sets of abstracts on specific topics, such as corrosion, or for specific materials. Several statistical tables can be prepared by computer from the data base information and over 200 copies of these tables have been distributed. Information is regularly supplied for the Failure Experiences feature of the DOE Materials and Components Newsletter, published by Battelle-Columbus.

Since the awarding of a contract to a commercial computer vendor, Data Center staff have been trained in the use of the DBMS. The Plant Performance Data Base has been completely transferred to the new DBMS and is operating on the vendor's computer. The design of the Materials Properties Data Base has been completed and tested on a small scale. The data are so varied in kind and style that a very flexible computer system is required to handle them. The numeric data include single-value numbers, ranges of numbers, and values obtained by digitizing data from graphs and histograms. Descriptive textual information is also accommodated in the computer. Along with the data the specific experimental conditions are stored as well as pertinent facts about the test procedure

used. Each material is designated not only by appropriate synonyms but also by the processing methods used, including the thermomechanical history. The data base is of such a design that it is open-ended with respect to the addition of new types of data as well as possible multiple entries from different sources for similar information. Full bibliographic reference information is also included. The design of the Materials Properties Data Base is compatible with the Plant Performance Data Base and the two are searchable simultaneously through certain common elements. These common elements are material names, component names, and performance or failure modes such as corrosion, erosion, etc. The simultaneous search capability of several data bases is a unique feature of the DBMS in use.

The major effort of the two Data Centers for the past year has been the completion of the first issue of a book, Construction Materials for Coal Conversion--Performance and Properties Data. At the beginning of the fiscal year, preliminary pages of the book were submitted to DOE. The final version comprises 600 to 700 pages. This first issue focuses on data for coal gasification plants, that form of coal conversion for which there is the largest body of materials data. The book contains information gained in practical plant experience as well as the results of materials research and testing programs. It deals with the information in the context of eleven separate component areas of the coal gasification plant, and draws from this information an indication of possible candidate materials of construction. Separate sections, still to be issued, will include extended data for the chemical, physical, and mechanical properties of the candidate materials. The book consists of loose-leaf pages so that increasing and revising the data can be done readily on a regular basis.

Materials Needs for Instrumentation in Fossil Energy
Subtask 8 of Task 12153

H. P. R. Frederikse

During FY81 the Ceramics, Glass, and Solid State Science Division prepared a report for the Fossil Energy Branch of the Department of Energy. This report is an assessment of materials research needed to solve instrumentation problems in various Fossil Energy Technologies (coal gasification and liquefaction, gas turbines, MHD, etc). The recommended program plan proposes four major research areas:

I. Materials Research for Sensors (erosion/corrosion, thermal/mechanical properties, and matrials for thermometers, flow meters, etc.)
II. Coal Characterization
III. Testing and Data
IV. Exploratory Research

The report was written by a group of five NBS staff members headed by H. P. R. Frederikse. The report is in its final stages of review and will be published as an NBS Internal Report in September 1981.

Crystal Data
Subtask 9 of Task 12153

A. D. Mighell, J. K. Stalick, R. J. Boreni

During the year, two major products were completed and are now ready for distribution to the scientific community. These products are the NBS Identification File and NBS*AIDS80 (written in collaboration with C. Hubbard). They can be used in any industrial laboratory for the identification and characterization of solid-state materials. Computer tapes in ASCII of the Identification File and NBS*AIDS80 are now ready for distribution to industrial laboratories.

The NBS Identification File (Version 1). This data file contains crystallochemical data on approximately 60,000 materials. For each material, the file contains the unit cell, cell volume, crystal system, space group, space group number, density, chemical name, chemical formula, and journal reference. The file is invaluable for compound identification because the unit cell is unique for most compounds. The NBS-Identification File has been sent to the NIH/EPA Chemical Information System (CIS) where it will be one of the component data bases. As such, it can be accessed anywhere in the U.S. and Western Europe via on-line computing techniques.

With the file, an unknown crystal can conveniently be identified by determining a primitive cell, finding the reduced cell, and checking the NBS Identification File.

The CIS software allows the user to enter any cell into the system, primitive or centered, and the identification will be carried out automatically. The NBS Identification File can also be distributed to the user as an ASCII tape. A computer printout of the tape would give a listing sorted on reduced cell that could be used directly for identification. The reduced cell required from the unknown can be conveniently calculated from any cell of the lattice with the program NBS*AIDS80 (see below). Also with the tape, laboratories can read the data into their own computers and develop independent identification procedures. Another approach would be to incorporate the data base directly into the computer that controls the single-crystal diffractometer. Thus, a check of the NBS Identification File can immediately be made as soon as a unit cell has been determined. A full set of data would then be collected for structure determination only if warranted. This approach is especially important as full sets of diffraction data are not uncommonly collected for structures already reported in the literature; worse yet, we have found a number of identical structures published more than once. Theoretical research on reduction theory was carried out in collaboration with A. Santoro of the Reactor Division. Preparation of the file was carried out in collaboration with the Cambridge Crystallographic Data Centre and with the Metals Data Center (Ottawa, Canada). Work on the file was sponsored by the NBS Office of Standard Reference Data and the NBS Ceramics, Glass, and Solid State Science Division.

NBS*AIDS80: A Program for the Critical Evaluation of Single-Crystal and Powder Data (with C. R. Hubbard). An efficient cooperation between the NBS Crystal Data Center and the International Centre for Diffraction Data (JCPDS) has resulted in the completion of Version 1 of a computer program, NBS*AIDS80. This is a sophisticated program that makes common procedures possible for data

base building, for the critical evaluation of crystallographic data, and for product generation. The program is written in FORTRAN, is modular in design, and contains many evaluation subroutines. A description of the program with respect to research applications is given in NBS Technical Note 1141 (U.S. Department of Commerce, National Bureau of Standards 1981).

The program derives from several years of experience in the computer-assisted evaluation of crystallographic data at the National Bureau of Standards. It is used routinely by the NBS Crystal Data Center for the analysis of crystallographic data in the preparation of the Master Crystal Data File. During the year, approximately 2000 new entries and approximately 10,000 entries from Vol. 4 of Crystal Data have been processed through NBS*AIDS80 and added to the Master File. This extensive testing has shown that the program works well and has enabled the correction of a few minor program bugs as well as the addition of new analysis routines (e.g., the automatic transformation of an unusual lattice centering, such as F-centered monoclinic cells). The program is also used by the JCPDS for the analysis of powder data for the Powder Diffraction File and it will be used by the Cambridge Crystallographic Data Centre to evaluate organic data for their file.

As there is a close relationship between single-crystal and powder data, the combined evaluation of single-crystal and powder data in a common format enhances the quality of data in both compilations. For example, the program permits the indexing of input powder data. Once the pattern has been indexed, the program compares the observed and calculated d-spacings, flags systematic absences if present, and calculates figures of merit. If the figures of merit are high, both the crystal cell dimensions and the powder pattern have a high probability of being correct.

The program has many research and analysis applications. It may be used in conjunction with routine diffractometry for identification and characterization of materials. For example, once unit-cell dimensions for a crystalline compound have been determined, the program can establish the probable symmetry of the lattice, the transformation matrix to the standard setting of the cell and space group, the calculated density for a check on the unit-cell contents, and the reduced cell needed to determine if the same or an isostructural compound has been previously reported in the literature.

The program evolved through invaluable contributions to the design and development by the following: L. Calvert of the Metals Data Center (Ottawa, Canada), E. Evans of the JCPDS Research Associateship at NBS, M. Holmany and F. McClune of the JCPDS, J. Rodgers and D. Watson of the Cambridge Crystallographic Data Centre, A. Santoro of the NBS Reactor Division, and R. Snyder of Alfred University. Work on the program was sponsored by the NBS Office of Standard Reference Data, the NBS Ceramics, Glass, and Solid State Science Division, and the JCPDS.

Prevention of Errors in the Literature. A brief survey of data in recent issues of Acta Crystallographica has revealed a number of serious errors. Fortunately, close ties are now being established with the editors of Acta Crystallographica. At the forthcoming IUCr meeting, procedures to prevent the incorrect determination of symmetry and to prevent multiple reporting of the same structure will be discussed. Two approaches are possible: (1) for the

journal editors to evaluate new crystallographic data by using NBS*AIDS80 and the NBS Identification File, and (2) for the journal editors to send selected data to the Crystal Data Center and to other centers for evaluation.

Crystal Structure Analysis and Materials Characterization
Subtask 10 of Task 12153

A. D. Mighell, J. K. Stalick, V. L. Himes

The combination of single-crystal diffraction methods with the Crystal Data File and with recent developments in lattice theory (collaboration with A. Santoro, Reactor Division) represents a unique capability for structure work and materials characterization. Consequently, collaborative projects with other groups at NBS, at FDA, and with university and industrial scientists have taken place during the year.

Structure Work. A variety of structural work has been carried out by V. Himes (an NBS-Catholic University Co-op student); a structural paper with A. Siedle of the 3M Company on a compound related to corrosion inhibition was written and published during the year; two structural papers (in press) in collaboration with S. Page and W. De Camp of FDA were written during the year; a structural study of $FeNb_3Se_{10}$ was carried out with R. Cava of Bell Laboratories and R. Roth of NBS; M. Lynch has obtained his M.S. degree from the University of Maryland on the basis of structural work done at NBS; a paper with G. Zon of Catholic University on a compound related to cyclophosphamide, a potent anti-cancer drug, was submitted to Acta Crystallographica; the Dental Group at NBS has collected several sets of data on the Syntex diffractometer.

A brief discussion on our most recently determined structure [$(FeNb)Nb_2Se_{10}$] will be given because of its relationship to $NbSe_3$ and the recent interest in this unusual type of material in physics and the materials sciences.

Our structural work shows that $FeNb_3Se_{10}$ (figure 1) is a new structure type composed of two $NbSe_6$ trigonal prismatic chains and a double chain of edge-shared $(Fe,Nb)Se_6$ octahedra, each parallel to the monoclinic b axis. The Fe,Nb disorder is confined to the octahedral chains, explaining the relatively small perturbation of the charge density wave which likely occurs in the trigonal prismatic chains as in $NbSe_3$. Efforts are presently underway at Bell Laboratories to synthesize other compounds in this structure type, in particular those of stoichiometry $(Metal)_2Nb_2Se_{10}$ which would not display metal atom disorder on the octahedral chains.

Materials Characterization. We have been working to link together the use of our automated Syntex diffractometer with the NBS Identification File for the characterization of materials. The combination is effective and in the future should prove to be a routine analytical procedure. During the year we have collaborated with a number of scientists on a variety of problems related to the identification or characterization of a given material. For example, unit cell determinations were carried out for the JCPDS-International Centre for Diffraction Data. Once the unit cell is determined by single-crystal techniques, a powder pattern of the material can be indexed unambiguously and a check of the Identification File by lattice-matching procedures may provide the equivalent of a chemical analysis. Often we find that scientists have materials that are

either chemically or crystallographically different than expected. The following cases referred to us serve as typical examples: (1) a sample labeled as one mineral at the Smithsonian was found to be a different mineral; (2) a crystal for which diffraction data were collected was different chemically than expected; (3) a supposedly polymorphic form of the drug carbamazepine was shown to be the same as the original form; and (4) NH_4SnF_3 was shown to have rhombohedral symmetry and not orthorhombic as reported.

Critical evaluation of data in the NBS Identification File is revealing that materials studied by diffraction techniques are commonly incorrectly characterized. Unit cells often define derivative sublattices, superlattices, or composite lattices. Application of reduction and matrix procedures (thesis work of V. Himes) has revealed that some compounds are reported in the wrong space group and crystal system. For example, rhombohedral symmetry can be missed by techniques routinely employed on modern diffractometers, indicating a major error in experimental strategy. New procedures to determine symmetry are now being devised and will be used to evaluate subsets of entries in the NBS Identification File and to determine the symmetry of new materials studied in our laboratory.

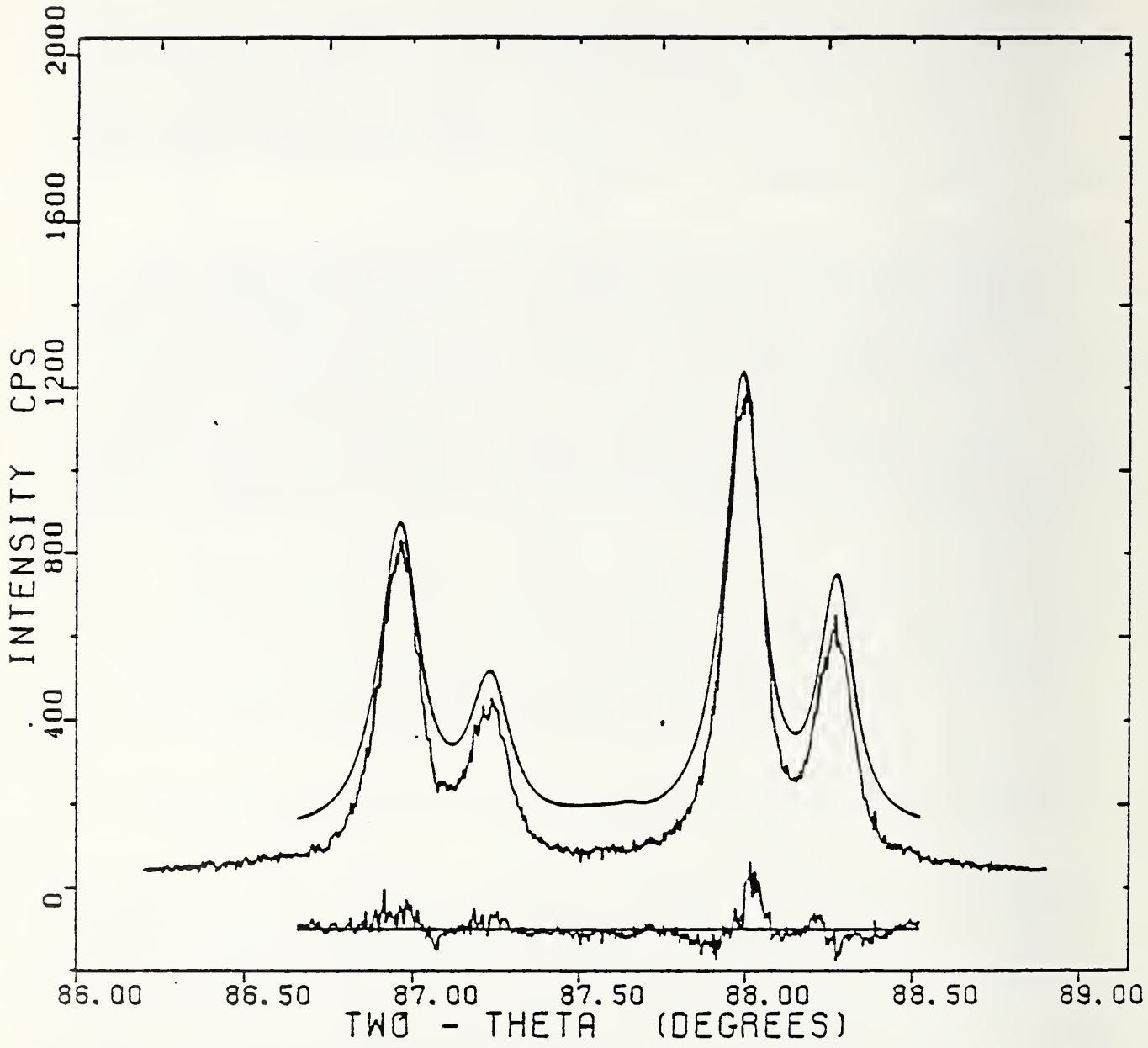


Figure 1. Example of the fit of four profiles of the form $P/(1 + ax^2 + bx^4)$ to observed data. The sum of the calculated profiles is the smooth curve offset from the raw data which exhibits random noise due to counting statistics. The difference between the calculated and observed intensity is offset below with a zero line superimposed.

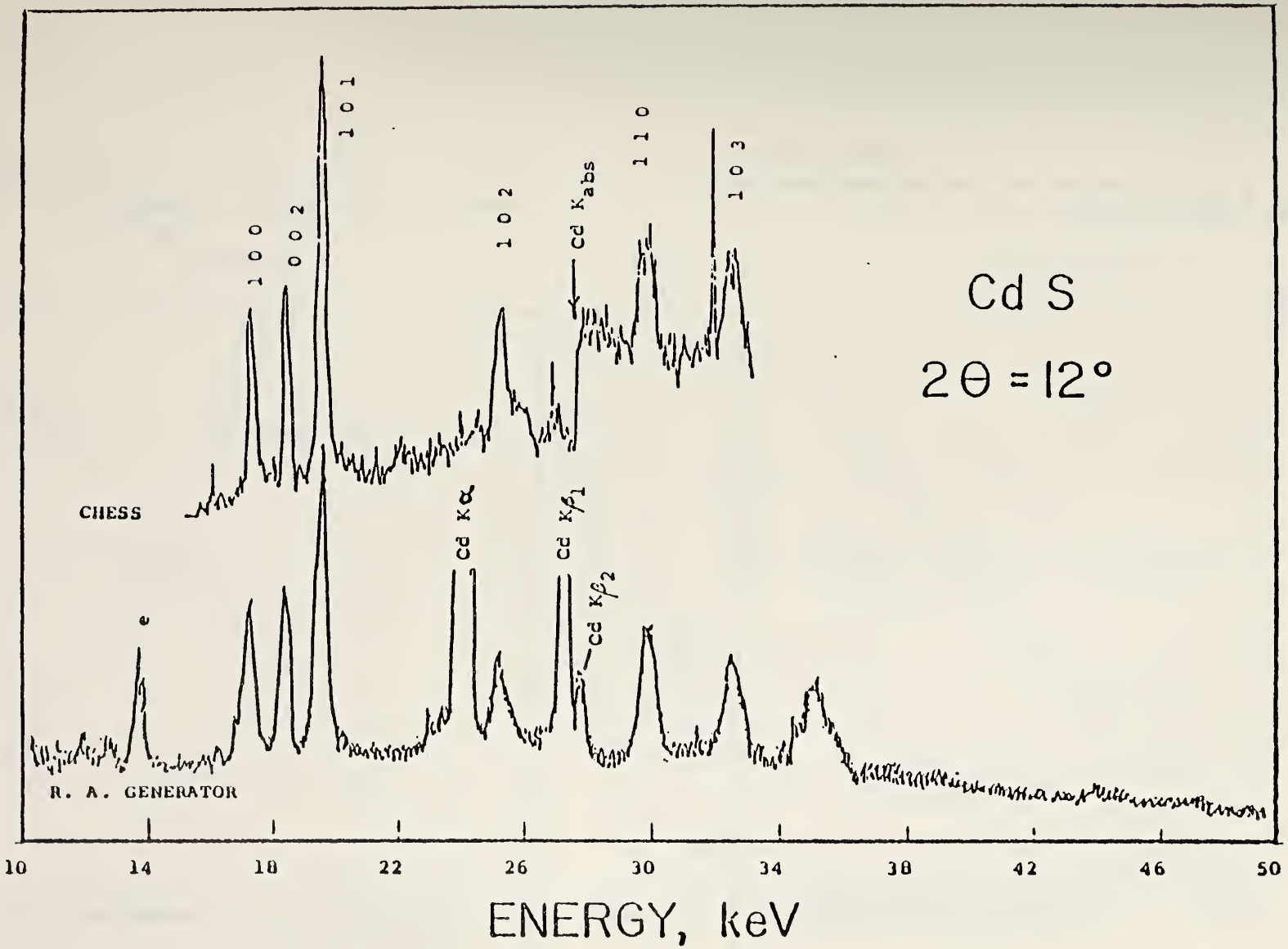


Figure 2. Powder diffraction patterns of CdS in the diamond cell recorded (a) with the wavelength scanning microdiffractometer at CHESS, and (b) with a solid state detector system and rotating anode generator at NBS. The peak intensity at CHESS was greater by a factor of 1.6×10^4 than it was on the rotating anode unit. Additional advantages include the elimination of lines due to specimen fluorescence and escape peaks.

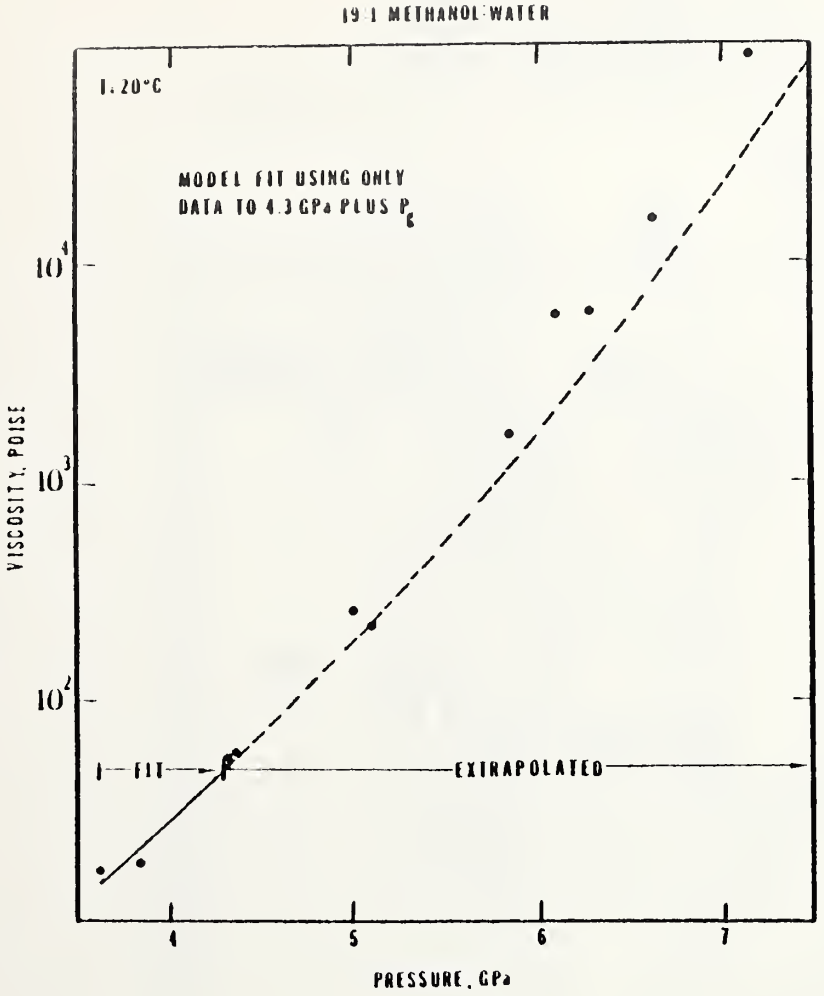


Fig. 3. Fit of critical point viscosity model to 19:1 methanol:water data using P_g = 12.1 GPa and data to 4.3 GPa.

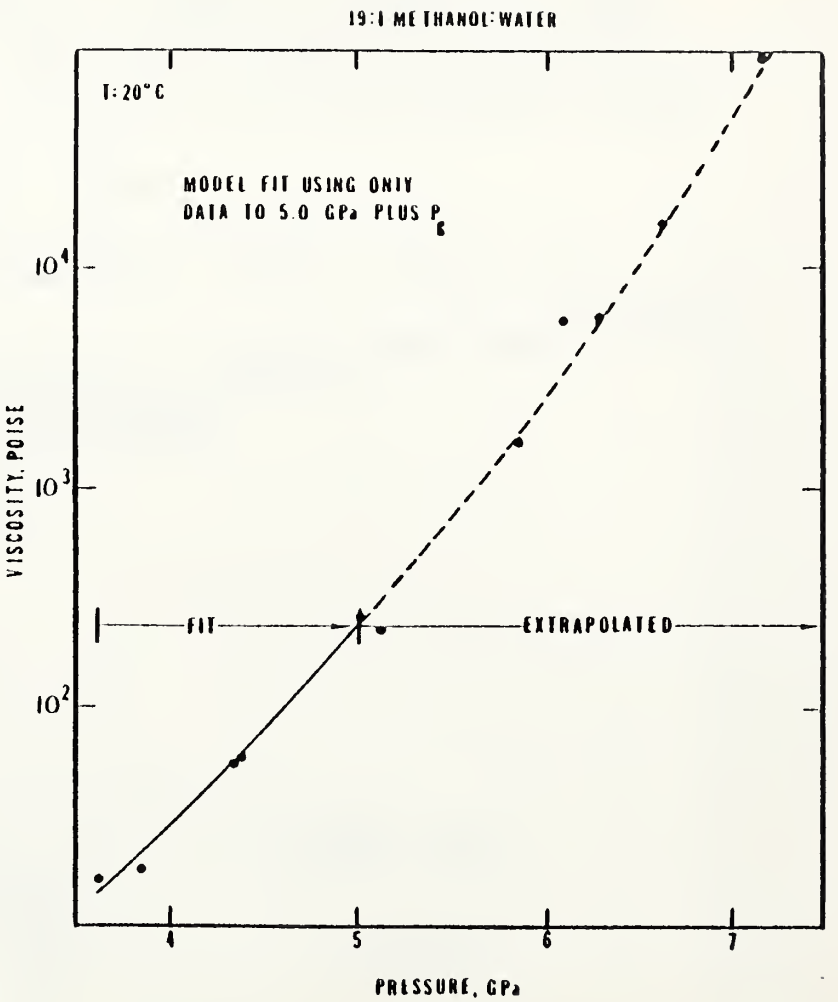


Fig. 4. Fit of critical point viscosity model to 19:1 methanol:water data using P_g = 12.1 GPa and data to 5 GPA.

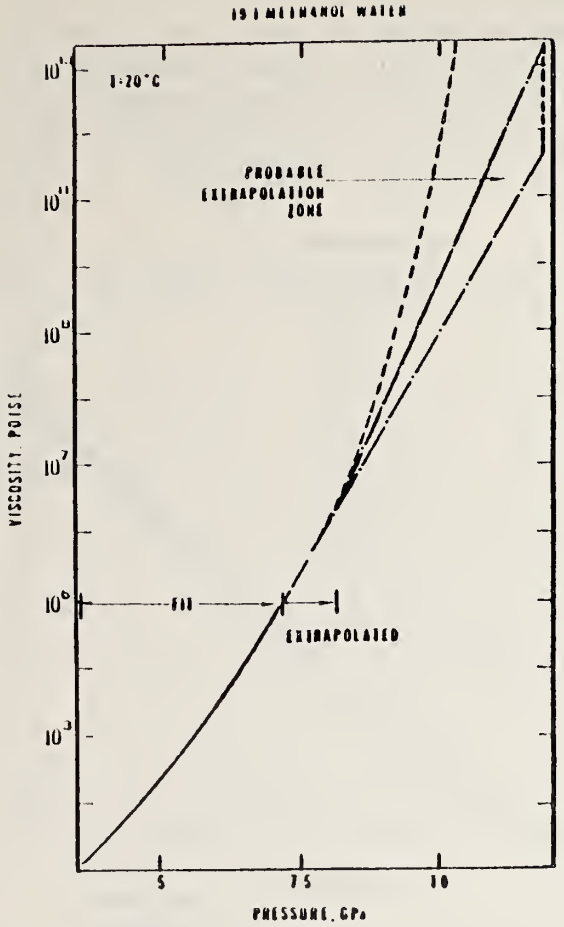


Fig. 5. Estimated range of reliable fit of the critical point viscosity model to 19:1 methanol:water data, and estimation of the viscosity to the glass transition.

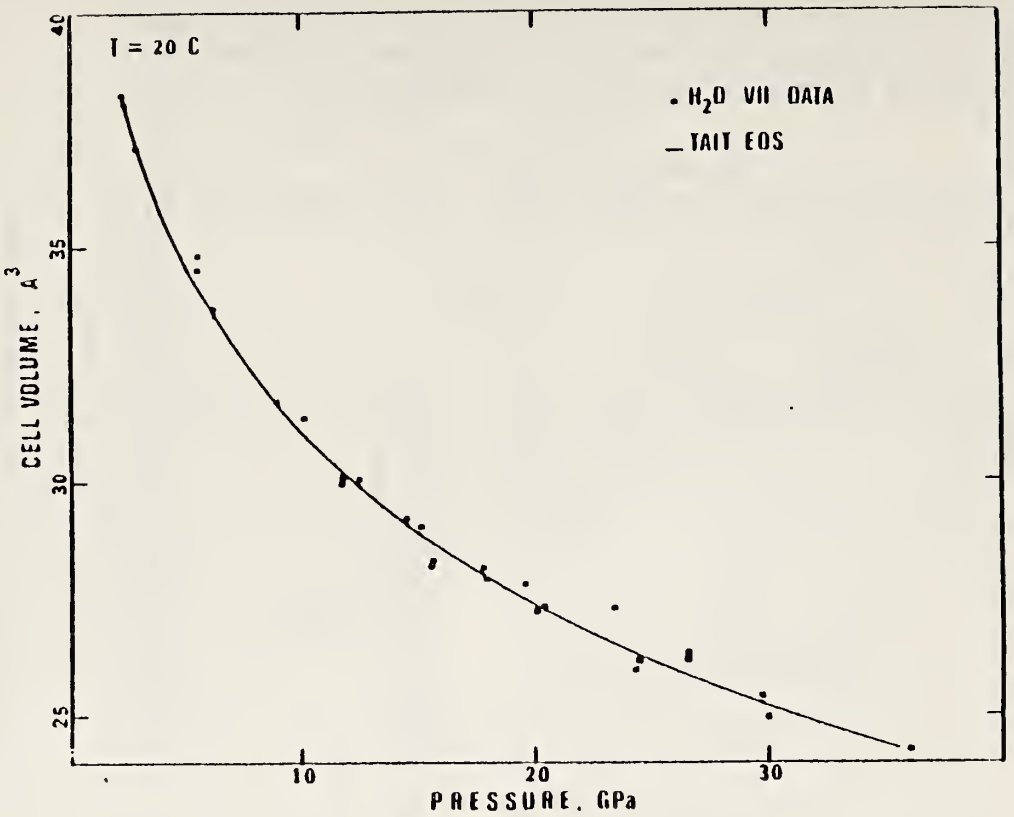


Fig. 6. Cell volume of H_2O VII vs pressure at 20 °C. The solid line is a fit of the Tait equation.

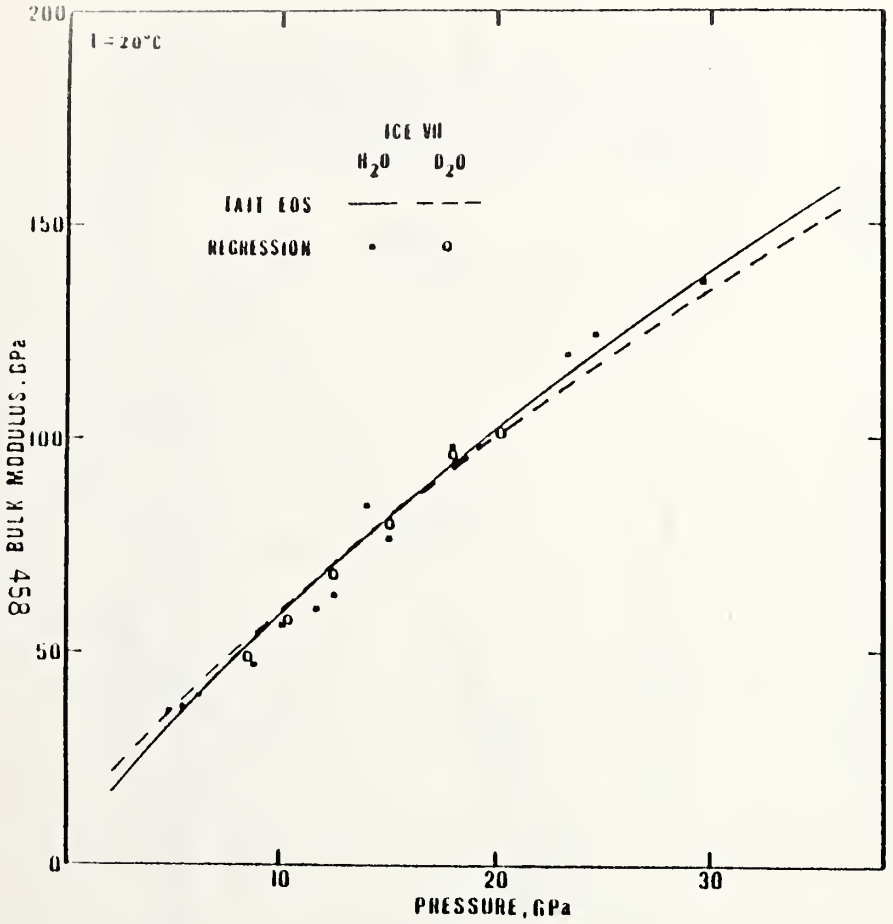


Fig. 7. Bulk moduli of H_2O VII and D_2O VII. The solid (dashed) curve results from the Tait equation fit to the H_2O (D_2O data. The solid square (open circle) discrete points result from piecewise regression analysis.

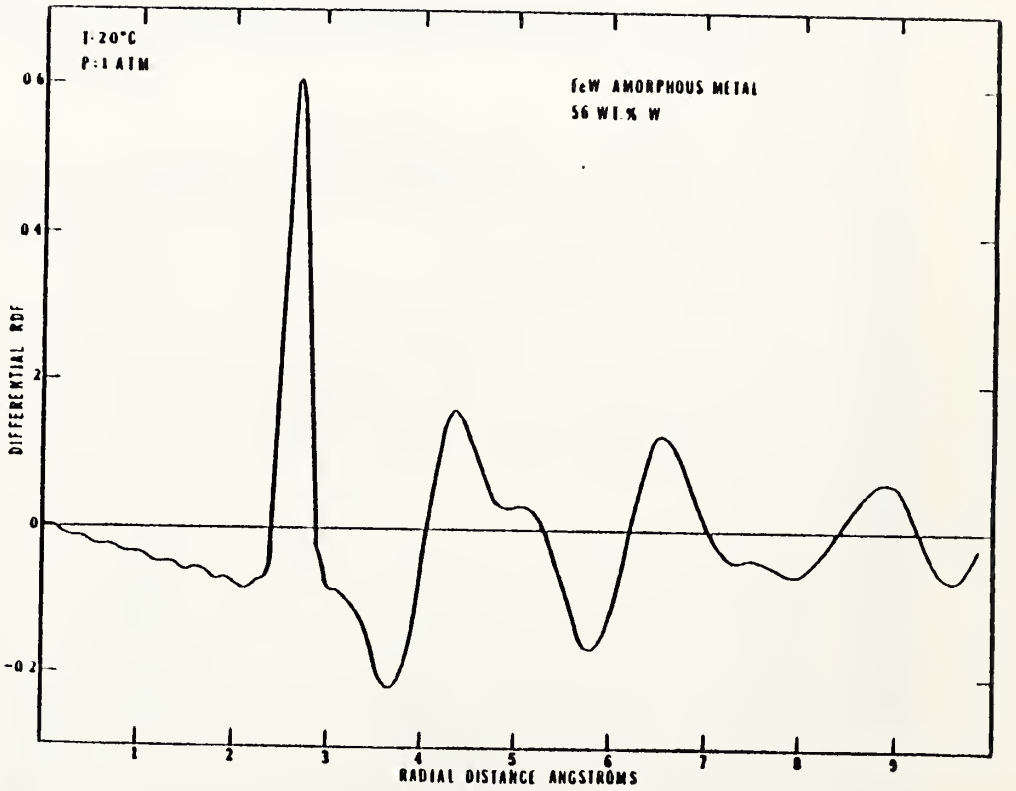


Fig. 8. The differential radial distribution function for amorphous FeW (56 wt. % W) at room temperature and pressure.

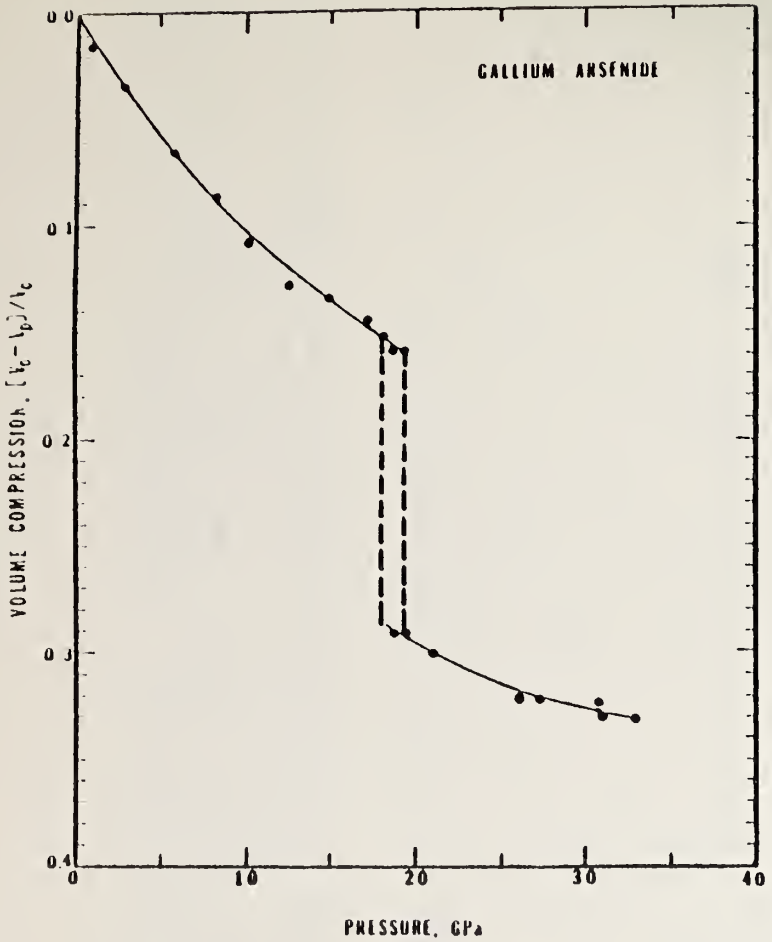


Fig. 9. Compression curve of gallium arsenide. The normal cubic phase found at low pressure transforms sluggishly to an orthorhombic phase in the region dilineated by the dashed lines near 18 GPa.

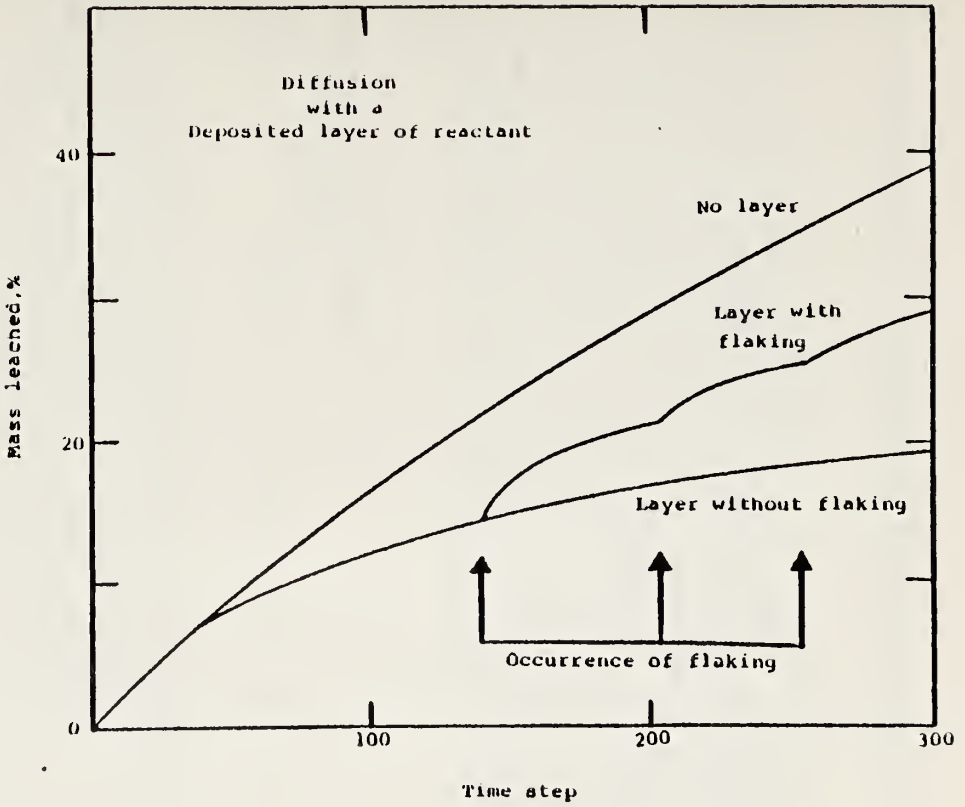


Fig. 10. Numerical simulation of the leaching of a substance A that reacts with substance B in the leaching solution to form a reactant C. Substance C deposits on the solid-liquid interface and then flakes off when its accumulated mass reaches a critical value. The percent of the mass of A that has been removed from the solid host is shown vs time.

PROPERTIES, STRUCTURE, AND STANDARDS FOR GLASS AND OPTICAL MATERIALS
Task 12154

The objective of this work is to develop techniques for synthesizing glasses and crystalline solids of special compositions, shapes, structures, and properties; to propose and improve methods for the measurement of chemical and physical properties of glasses and crystals in bulk and in thin film form (e.g., solubility, evaporation from solid and liquid glasses; homogeneity and purity of amorphous films); to study relationships between properties, structure, and constitution; to assist the glass, and optics industries; to provide standard reference materials of use to glass-related and other industries; to characterize glass and crystalline materials for use as optical components and solid state electrodes; to measure refractive index and its change with temperature and pressure, to use Raman spectroscopy for the analysis of crystals and thin films, and to apply light scattering and microwave loss techniques to the detection of surface imperfections.

Physics and Chemistry of Glass
Subtask 1 of Task 12154

D. H. Blackburn, D. J. Cronin, W. K. Haller, D. A. Kauffman, D. M. Sanders, J. T. Wenzel

Glass is a solid material characterized by a unique combination of properties and distinct production technologies. The bulk volume of glass is used for architectural purposes, packaging, building insulation, and optical and electronic components. These traditional glass products are produced by a well-focused industry. Thermoplasticity, chemical durability, optical transparency, dimensional stability, and electrical resistivity are among the most important properties of glass. These properties are not only the basis for the above-mentioned more traditional applications of glass but also of such more novel applications as solar mirrors and collectors, lasers, fiber-optical devices, host for nuclear waste, electronic substrates, and containment shells for nuclear fusion gases. Several abundant industrial by-products and natural materials are in the glassy state: fly-ash, coal slags, blast furnace slags, obsidian. Glass as a solidified liquid permits production of large pieces with a homogeneity not available from any other materials. Its unique structure permits compositions spanning a wide range of stoichiometries. The latter two properties and the fact that glass can be formed into many shapes ranging from large bulk pieces to fibers, microspheres, and films, has made glass a favorite material for analytical standards. There are many defense- and national security-related applications of glass. NBS is considered as a national center for glass science and technology in the United States and its Glass Group has a particularly close relationship with other Government agencies and the U.S. industry.

A number of fundamental physico-chemical phenomena which are an essential part of glass-formation, such as thermodynamic activities in melts, melt crystallization, liquid/liquid phase separation, and viscosity are investigated by NBS. The results of these investigations are discussed below. In addition, we continue to respond to a large number of glass-related inquiries from the glass-using, glass-producing industry, the general public, Government agencies, universities, and research laboratories. These groups look upon the NBS as a

national focus in glass technology and the type of inquiries reflect, therefore, on certain national trends. We observed a noticeable upswing in inquiries related to glass as a component in solar energy devices (solar cell covers, flat-plate and focused-tube receivers). These inquiries come either from companies having entered the field of solar energy or from users or prospective users of such devices. We also note an upswing of inquiries relating to microelectronics (glass substrates, glass encapsulants, thick film coatings). A good number of inquiries come from municipalities, companies, and individuals trying to be responsive to Federal or State regulations such as those dealing with architectural glazings or eye-glass safety. Other inquiries have come from such places as the Department of Justice, U.S. Customs Services, and the International Trade Office and deal with legal definitions of technical glass terms. Organizations, such as Municipal Port Authorities, Voice of America, the CIA, the Naval Research Laboratory, and Air Force Avionics Laboratory required assistance in special glass applications. Lawyers and private individuals either directly or through their Congressmen, inquired about legislative information or help on failures of glass products. Members of the Glass Group also reviewed several applications for duty-free import of glass products for technical details and availability of suitable alternative products from U.S. suppliers.

Vaporization from Boron-Containing Glass Melts. Sodium borosilicate vaporization is of interest to the glass industry because compounds containing boron and sodium appear to have substantial vapor pressures under industrial conditions. These vapors are quite corrosive to tank refractories and the loss of boron is of concern because of its increasing expense and scarcity. The addition of small amounts of boron to soda-lime-silica glass lowers melting and fining temperatures without changing viscosity-temperature characteristics in the glass forming range, potentially leading to substantial energy savings. Boron is also used as a major component in glasses having superior chemical durability for medical fluid containers, chemical lines, and glass fiber thermal insulation. These glass compositions are also resistant to thermal shock, making them useful for applications such as laboratory and kitchenware. In our recent studies, data taken with the stirrable high temperature transpirator (STA), had been used. Analysis of vaporization data had shown that the vapor above the equimolar sodium borosilicate melt was non-stoichiometric. The two-species vaporization model, developed during the previous year, was cast into a form which allows the extraction of separate equilibria constants K_1 and K_2 for the reactions:

$$(1)\quad H_2O\ (g) + B_2O_3\ (l) = 2HBO_2(g)\quad K_1$$

$$(2)\quad 3H_2O\ (g) + B_2O_3\ (l) = 2H_3BO_3\ (g)\quad K_2$$

The activation energy E_1 for reaction (1) was determined from temperature-dependence experiments to be 40 kcal/mol. These three thermodynamic quantities (E, K_1, K_2) agree well with JANAF thermochemical table predictions.

Calculations were also extended on the 1:1:4 sodium borosilicate vaporization. They demonstrate that although sodium oxide and boric oxide separately show extreme non-ideal solution behavior, the compound formed from the two, sodium borate, behaves nearly ideally. The vaporization from the sodium borosilicate melt may be attributed solely to the inherent vapor pressure of sodium borate.

A paper describing boron and sodium vaporization in a boric oxide and sodium borosilicate glass melt has been accepted for publication in "Physics and Chemistry of Glasses."

Vaporization from Strontium-Potassium Containing Silicate Glass Melts. This system is of theoretical importance to the verification of a multi-component diffusion model developed by Professor A. R. Cooper of Case Western Reserve University. Several feasibility experiments were made during the summer of 1980 by a student guest worker (M. L. LaRosa) on one binary and one ternary composition in the system. The tentative conclusion was that the potassium silicate reactively vaporizes with water vapor to form potassium hydroxide gas above the melt. In the ternary system the strontium vapor pressure is too low to measure using reasonable STA collection times. In both experimental series the potassium analytical technique lacked sufficient sensitivity and needs to be improved.

Nucleation Kinetics in Li_2O-$2SiO_2$ Glass. A fundamental prerequisite for making technical glasses is the ability to undercool melts to the solid state without interference by crystallization. Similarly, such composites as recrystallized glasses (glass-ceramics) are the result of carefully controlled nucleation and crystallization. The thermodynamics and kinetics of nucleation and crystallization as well as the morphological connection between nuclei and crystals are therefore of continued interest to glass science. Published experimental observations regarding platinum-induced crystallization are in contradiction of accepted nucleation theories. We, therefore, undertook a detailed study of nucleation kinetics. Over the past year we refined experimental techniques to measure rates of nucleation of crystal growth. Systematic data on nucleation rate as function of temperature and platinum concentration have been collected.

Cooling Induced Luminescence in Terbium Phosphate Glasses. As part of an investigation into the lasing behavior of a $Tb(PO_3)_3$ glass it was observed that an intense green emission was produced when the molten glass was cast onto a metal slab from a starting temperature of 1400 °C. For a 100 g melt the emission lasted approximately 20 seconds. Later spectroscopic measurements showed the same effect to occur with $Eu(PO_3)_3$ but the emission is in the red portion of the spectrum and not easily seen because of the blackbody radiation.

Further experimental work showed that rapid cooling was required to produce this form of luminescence. The cooling rate necessary is related to the starting temperature. For cooling in water at a rate of 500 °C/s the effect could be observed with a starting temperature of 850 °C. The green emission for $Tb(PO_3)_3$ was found to correspond to the emission lines of Tb^{+3} luminescence. Small changes in terbium concentration about $Tb(PO_3)_3$ had no effect. Addition of univalent ions, such as Mg, Al, or Na, had no effect. However, addition of variable valence ions, such as Sb or Ce, completely quenched the effect, although the glass would still show characteristic Tb^{+3} fluorescence under a UV-light source.

Further experimentation also showed that bubbling oxygen through the melt would quench the effect completely, but that it could be rejuvenated by remelting and bubbling CO or NH_3 through the melt.

These results show that the effect is sensitive to both cooling rate and the overall oxidation-reduction balance of the melt. The emission may be the result of a thermally induced shift in oxidation state, the exact nature of which has not been determined. A paper on this most unusual phenomenon has been submitted to Nature.

Viscosity of Melts in the $CaO-MgO-Al_2O_3-SiO_2$ System. The work is being carried out in conjunction with Dr. C. M. Scarfe of the University of Alberta, Canada, and the Geophysical Laboratory of the Carnegie Institution of Washington.

This oxide system is of interest to geologists as a model for basaltic magmas and lavas, to the glass technologist because it forms a number of useful alkali-free glasses which may have potential for electric insulators and glass fiber insulation. Abundant waste materials from several ore-using and ore-processing industries, such as slags and coal-ash, are furthermore related to this composition. There is an interest in having accurate viscosity data for this system for modeling purposes and correlation with melt structure information that is of interest to both glass technologists and geologists.

It had been previously suspected that certain viscosity data in the literature were in error. The compositions studied ranged from $CaO-MgO-2SiO_2$ (Diopside) to $CaO-Al_2O_3-2SiO_2$ (Anorthite). The composition variations being a substitution of Al_2O_3 for MgO on a mol-for-mol basis. The viscosity results show a nearly linear increase in log (viscosity) as mole percent Al_2O_3 increases. Calculated activation energies also increase smoothly going from Diopside to Anorthite. This agrees with the interpretation of an increasingly polymerized melt as Al_2O_3 is added.

It also agrees with the spectroscopic evidence of Scarfe, et al., that indicate that the IR spectra of the intermediate composition can be constructed by simple combinations of the spectra of the end members.

In connection with the viscosity measurements, a study was done to determine the precision and accuracy of the high-temperature, rotating-spindle viscometer. Several data-fitting procedures were employed and a glass viscosity SRM was used as the calibrant. It was found that the precision of measurements on a single melt as a function of temperature was better than 1 percent; and that the precision of measurements on separate melts (for example, melts of a compositional series) is about 1 to 2 percent. The accuracy of viscosity measurements is about 4 percent, except for very fluid melts (85 poise). A paper on the calibration procedure has been submitted for publication in the NBS Journal of Research.

Dynamic Synchrotron SAXS Investigation of Subliquidus L/L Phase-Separation in Glasses. This is a collaborative project with G. B. Stephenson and A. I. Bienstock of the Synchrotron Laboratory at Stanford University. The purpose of this project was to investigate the feasibility of obtaining dynamic morphological information on the microstructure development of undercooled melts while being held at temperatures close to the critical immiscibility temperature. Structural information on the nucleation/growth mechanism in phase-separating glasses are fundamental to the understanding of liquid theory, but also to the understanding of important technological phenomena. They relate to durability deterioration in glasses and to structure development in recrystallized-glass type ceramics. Such information was, in the past, gained from postmortem examination of quenched glass samples.

The very high x-ray intensities available at the synchrotron ring reduce required exposure times for small angle x-ray scattering investigations and invite in situ observation of phase separations.

Most of the past year was spent in solving instrumental problems associated with the x-ray focusing and monochromatization system as well as with the detector system. The search for a suitable glass system with high scatter contrast, slow phase separation, and close to equal-phase-volume characteristics was continued. Glasses from the $Na_2O/B_2O_3/SiO_2$ system have the above properties except that they lack high scatter contrast. Glasses in the $BaO/SiO_2/R_2O$ system (R = alkali) were investigated for the location of immiscibility surfaces, but investigations were terminated. A barium-containing optical glass which had been found to slowly phase separate in a study conducted several years ago (Haller, Simmons, Napolitano, J. Amer. Cer. Soc. 54, 299, 1971), was investigated by SAXS in the quenched state. No x-ray scatter peaks were found, indicating that the visible optical scatter stemmed from relatively large spheres present in small concentrations. Since it was not possible to do a systematic immiscibility surface study in a system with heavy elements, it was decided to continue with the weakly-scattering but otherwise well-explored $Na_2O/B_2O_3/SiO_2$ system [Haller, Blackburn, Wagstaff, Charles, J. Amer. Cer. Soc. 53, 34 (1970)]

Glassy Multicomponent Films
Subtask 2 of Task 12154

D. M. Sanders, E. N. Farabaugh, M. E. Wilke, (S. A. Hurwitz, K. M. Summers, A. Tegtmeyer)

During the last year, we have continued to develop a facility for the preparation and characterization of metallic and dielectric thin films. The deposition chamber part of this facility permits the preparation of thin films by codeposition from multiple electron beam and resistively heated evaporation sources. In addition to overall system development, we have acquired extensive experience in electron beam evaporation techniques which has permitted us to produce thin films having high energy laser damage thresholds similar to those obtained by commercial thin film vendors. This represents a two-fold improvement over earlier efforts. Such background will be essential for carrying out the experiments to be described in the next sections.

System Improvement. During the past year we have improved techniques for substrate heating so that BK-7 glass substrates can now be heated to 450 °C in the presence of oxygen at pressures of 1×10^{-4} mbar. This compares with previous heating techniques which were limited to 200 °C and 1×10^{-6} mbar O_2. This improvement will allow us to deposit ceramic coatings having lower intrinsic stress and better chemical stoichiometry.

A bakeout system has now been installed on the carousel-loadlock assembly to improve the ultimate vacuums possible in anticipation of fracture experiments to be carried out in that chamber.

The apparent film thickness indicated by the quartz crystal monitors was calibrated using scanning electron microscopy and stylus technique. A knowledge of the absolute film thickness is necessary for the studies of metal passivation discussed below.

The hardware for computer automation of the surface analysis subsystem has arrived and awaits shipment of the software. When completed, the computer automation will permit faster acquisition of data with a superior signal-to-noise ratios. In addition, peak deconvolution will be possible permitting the separation of overlapping ESCA and ISS peaks. This capability is particularly important for studies which involve the use of Electron Spectroscopy for Chemical Analysis (ESCA) for the determination of the state of chemical bonding.

Preliminary experiments were carried out using the Ion Scattering Spectroscopy (ISS) mode of the surface analysis subsystem. Since this is the technique which is most surface sensitive, analyzing only the uppermost monolayer, it promises to be useful in studies of adhesion, lubrication and wear.

Non-Crystalline Optical Coatings. Dielectric coatings currently are the weakest part of the high-energy laser systems used for energy and weapon research. For several years we have been working on a project to identify the cause of this weakness in hopes of improving system performance with minimal additional cost. While some evidence exists in the thin film laser damage literature that amorphous coatings have somewhat greater damage resistance than their polycrystalline counterparts, this evidence is not conclusive and deserves further study. To this end, homogeneous mixture films of ZrO_2-SiO_2 were produced to provide a systematic variation in film crystallinity. We characterized the extent of this crystallinity using x-ray diffraction and subsequently shipped the coatings to Lawrence Livermore Laboratory (LLL) for laser damage evaluation. Initial results indicate an overriding influence of external factors. While the damage thresholds represent a substantial improvement over our own previous efforts, our films are now comparable with those prepared by widely-experienced commercial vendors.

In the next year, efforts will be made to correlate the results obtained using the surface analysis techniques with laser damage thresholds. In addition, a cooperative effort has been started between the Avionics Lab at Wright-Patterson Air Force Base, this Laboratory, and LLL to establish if there is any correlation between surface roughness and laser damage resistance. Finally, we will develop techniques to produce gradient refractive index coatings using multiple source evaporation in hopes of eliminating laser damage caused by the absorption and scattering at the substrate-film interface.

Thin Film Stress Corrosion. In order to predict long-term mechanical behavior of ceramic systems under load, it is necessary to understand the nature of the chemical reactions which lead to time-dependent brittle fracture. Such reactions are poorly understood, but may involve the stress-dependent interaction between ceramic surfaces and hydrogen or water vapor in the atmosphere. In order to better understand these reactions we have initiated a study to determine the ability of surface analysis techniques, such as Electron Spectroscopy for Chemical Analysis (ESCA), Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectroscopy (SIMS), and Ion Scattering Spectroscopy (ISS) to detect hydrolytic reactions with freshly-fractured ceramic surfaces.

The first phase of the program, carried out last fiscal year, was designed to establish the feasibility of using x-ray photoelectron spectroscopy for the study of hydrolysis reactions in ceramic materials. For expedience, a diamond

stylus device was developed to scratch the surfaces of ceramics such as silica in the preparation chamber of the Leybold-Heraeus surface analysis system. This scratching was done in vacuums of at least 1×10^{-9} mbar. During narrow 20 eV scans of vitreous SiO_2, the oxygen 1s peak appeared to split with measurements made using small (more surface sensitive) takeoff angles for the photoelectrons. This result implies that the technique can distinguish between surface and bulk oxygen. Exposure of the freshly scratched surface to water vapor introduced further changes in peak position and shape. While these preliminary results are encouraging, more measurements will be required using computer analysis and electron gun charge compensation to draw definite conclusions.

While awaiting delivery of the computer software and electron flood gun for charge compensation, other methods for producing pristine surfaces in ultrahigh vacuum conditions were explored. Since 1 cm^2 of freshly fractured surface is required to carry out angle resolved ESCA, it was necessary to use the NBS designed loadlock-preparation chamber for vacuum fracture of bulk ceramic specimens. This, in turn, required the design and construction of a bakeout system for that chamber to improve the vacuum in that chamber. This installation has been successfully accomplished. In addition, techniques for propagating flat cracks at least 1 cm^2 wide in the vacuum system were developed and demonstrated. The freshly fractured surfaces so produced were then transferred to the analytical chamber for characterization.

Recently, both the charge compensating flood gun and the software for the surface analysis system computer automation have been delivered and await installation by the manufacturer. Once this is done, surfaces of SiO_2, MgF, and Al_2O_3 will be produced and characterized in their pristine states using ESCA, angle resolved ESCA, AES, ISS, and SIMS. The surfaces will then be exposed to water vapor and organic vapors such as ammonia hydrazine and re-analyzed to search for changes.

Assuming a positive result, the next phase of the program involves the preparation of a ceramic thin film on a cantilevered substrate under ultrahigh vacuum conditions. This film will be characterized using the surface analysis techniques mentioned, reacted with water vapor and various other atmospheres under varying levels of stress produced by deflection of the substrate, and subsequently analyzed for any changes produced. If stress dependence of either reaction rate or type of reaction is found, such information would greatly add to the understanding of delayed fracture in ceramic materials. This understanding would provide a basis for superior predictions of the mechanical properties of ceramics under stress.

This program is being carried out in cooperation with the Fracture and Deformation Division (562).

Protective Films on Metals. Non-noble corrosion resistant metals owe their resistance to adherent reaction layers which form an effective diffusion barrier protecting the underlying metal. In spite of the importance of these passive layers, the relationship between structure, mechanical properties, and protective ability is still poorly understood. One metal which lends corrosion resistance to iron alloys under a wide variety of environments is chromium. If the exact nature that chromium plays in increasing durability could be established, perhaps substitute alloying materials could be found. Such a substitution would be highly desirable since chromium is imported.

In order to explore this protection mechanism, we will attempt to produce synthetic passive films on iron substrates by a process of codeposition. These films will be characterized with respect to their crystallinity and chemical bonding and the results of this characterization will be correlated with the ability of the films to protect their underlying substrate. Glassy film facility improvements described in the last section were also required for the present study. Initial attempts at passivation film evaluation were also carried out. This project is carried out in cooperation with the Metal Corrosion Group.

Lubrication of Metals. The feasibility of using the surface analysis instrumentation which is part of the Glassy Films Facility to study problems in lubrication of metals will be explored. This work will be done in cooperation with the Tribology Group.

Mechanical Properties of Thin Film. A study of high temperature creep of unsupported thin films using the bulge technique has been initiated. Films as thin as 2000 Å have been produced and separated from their substrates. Further development work will be necessary to demonstrate feasibility of the bulge technique for creep measurement, first at low temperature, and then at temperatures in excess of 1000 °C.

Standard Reference Materials for the Glass Industry
Subtask 3 of Task 12154

M. J. Cellarosi, D. J. Cronin, W. K. Haller

Liquidus Temperature SRM. This standard (SRM 773) was issued for sale last year. A full description of the work leading to certification can be found in previous Panel reports.

Viscosity SRM. The viscosity of a glass is important in industry as a quality control indicator because of its sensitivity to compositional fluctuation and its importance in the forming process. It is also of interest in research studies as it is frequently related to other properties and structural behavior. SRM's for glass viscosity are therefore not only used by the glass industry but also by university and other research laboratories.

The NBS stock of one of the most widely used glass SRM's, #710, a soda-lime-silica glass, is reaching the point where it will soon be necessary to issue a replacement. In anticipation of this, a new high temperature precision viscometer is being constructed for use in the certification process.

A new viscometer was designed using commercially available torque measuring equipment and a furnace designed at NBS. Initial calibration of the torque measuring equipment indicated that it would be satisfactory for SRM work. Additional experimental work was carried out using a mechanical torque converter in an attempt to extend the range of the instrument to lower viscosities. This work was only partially successful. The system worked as expected, but the introduction of the mechanical torque converter results in measurement uncertainties that are unacceptable for the present instrument.

Further consideration of the viscometer design indicates that modification of the original design will result in an instrument that will give superior results while reducing experimental difficulties. It is expected that the instrument will be ready in sufficient time for calibration of the SRM 710 replacement.

Dielectric Constant SRM. This work is carried out in collaboration with ASTM Committee C14.04 on Physical and Mechanical Properties of Glass.

This SRM is needed to upgrade, standardize, and calibrate the measurement systems employed by both producers and users of glass. Its need had been established by a survey conducted by NBS on behalf of ASTM. This SRM is also expected to be of interest to the plastic industry as the inherent long-term stability of glass is superior to that of plastic for calibration purposes.

Glass is used extensively in electrical/electronic applications. Examples of such applications are: envelopes for electronic devices, substrates, encapsulation, microwave windows for electromagnetic waves, capacitors, insulation, etc. An SRM for this property will support the anticipated expanding role of glass in this wide range of applications.

The SRM is also expected to help in energy conservation efforts (e.g., low loss insulators and dielectrics), and serve as a valuable material for the development and testing of theories of dielectrics. Also when adequate correlation data are available, the SRM may be used to indicate other characteristics of a glass, such as, dielectric breakdown, moisture content, deterioration, etc.

NBS heads an ASTM task force of industrial and academic laboratories for interlab comparison activities, and for studies that increase test precision, and to develop standard methods. During the year, interlab measurement activities were continued. Several discrepancies in procedures and calibrations were resolved. This work is almost completed. Viscosity SRM 711 samples were used in these measurements. Statistical analysis of the data indicates that SRM 711 will qualify for Dielectric Constant SRM status. A new test cell/fixture had been developed by NBS to minimize errors due to inductance/capacitance and stray factors. These techniques were evaluated and accepted by ASTM for inclusion in standard procedures.

Glass High-Temperature Resistivity SRM. For reasons of improved energy utilization, pollution reduction, increased productivity necessitates development of an SRM for this property. This task is now listed as a priority by ASTM Committee C14.91 on Glass SRM development. Accurate knowledge of resistivity vs temperature dependences will help the design of advanced melting process equipment and aid energy management to reduce power costs.

NBS leads an ASTM task group on interlab testing, and to develop standard methods for measuring glass resistivities in the molten range. A second round robin is now in progress with SRM 711, which is already certified for electrical resistivity in the lower temperature ranges. SRM 711 will also be certified for dielectric constant and loss characteristics, so this single glass will cover a broad range of electrical properties. NBS statistical analysis of the first round robin indicated serious measurement discrepancies in the very high

temperature range. Tentative procedures utilize high-temperature viscosity apparatus. In-house research by NBS is being planned for FY82 to set up equipment and to carry out calibrations.

Glass Standard Reference Materials Liaison. The Glass Group maintains broad relations with the glass industry, R&D organizations, and academia concerning the progress of science and technology in the field of glass, and present and future needs in standardization. Active participation is extended to various standard organizations. In particular, the Glass Group is encouraged by both producers and users of glass to play leadership roles in various standards activities. Examples of such leadership roles are offices held in ASTM Committee C-14 on Glass and Glass Products and in the International Commission on Glass.

Analytical Glass Standard Reference Materials
Subtask 4 of Task 12154

D. H. Blackburn, D. A. Kauffman

Glass Standards for Small Particle Analysis. Glass has many properties which make it uniquely suitable for analytical standards in microbeam analysis. Since there are numerous oxide glass-forming systems, it allows flexibility in selecting a glass matrix to minimize interfering and overlapping responses which can confuse interpretation of analytical data. Further, glass is essentially structureless and can be made extremely homogeneous even with a large number of elements present. However, one of the most unusual features is that glass can be fabricated into a variety of shapes and sizes from the same parent glass melt of known composition. Bulk specimens of millimeter or larger size can be fabricated by conventional grinding techniques. Continuous fibers can be formed in kilometer lengths with diameters as small as 3 microns, spheres ranging in size from 100 microns to submicron diameters and thin films below 2000 Å in thickness can be produced.

The Glass Group has developed a considerable number of glass compositions which were produced in forms of cubes, microspheres, films, and fibers. The work has resulted in the issuance of Research Materials and Standard Reference Materials for microchemical analysis. D. S. Simons and B. B. Thorne have compiled a book listing 97 of these glasses. Further expansion of this work will require glasses that contain radioactive elements such as uranium, thorium, and their natural daughter products. This work would require the construction of appropriate facilities for the safe handling and production of these materials. Another area of possible expansion will be the preparation of stable isotopic standards Preliminary work has been completed on the preparation of isotopic lead-silicate glass spheres for the calibration of ion microprobe and laser microprobe mass analyzers.

Two publications have been published by NBS personnel with the help of the members of the Glass Group: (1) Ion Microprobe, Ion Microscope, and Laser Microprobe Mass Analyses of Particulates by David S. Simons in Microbeam Analysis, 1980, edited by David B. Wittry; and (2) Ion Microprobe and Ion Microscope Analysis of Particulates by D. S. Simons and D. E. Newbury in the Proceedings of the American Society for Mass Spectrometry, 1980.

Other publications on particle analysis using glass microspheres made by the NBS Glass Group: (1) Quantitative Particle Analysis in Electron Beam Instruments, John A. Small, International Journal of Scanning Electron Microscopy, 1981; and (2) Errors Observed in the Analysis of Particle Mixtures by Overscanning, R. L. Myklebust, J. A. Small, and D. E. Newbury, International Rev. of Scanning Electron Microscopy, 1981.

Analytical Standards for Biological Materials. Work is in progress to extend the use of glass analytical standards into biological applications. This requires glasses with a low Z matrix similar to that of animal tissue. Lithium borate and other borate glasses have been explored for suitability for this application. Considerable progress has been made in this cooperative effort with groups at the National Institutes of Health. Progress in this work will be presented in a talk at the 16th Annual Conference of the Microbeam Analysis Society, July 13-17, 1981, at Vail, Colorado, and a publication entitled "Low Z Glass Standards for Biological X-ray Microanalysis" by C. Fiori and D. H. Blackburn is being submitted to the Journal of Microscopy. Glass fibers similar in size and trace elements to the retinal rods in animal eyes have been produced as an aid in research in the sight process. Two further publications are in progress on this subject: X-ray Microanalysis of Rod Shapes with Applications to Cytology and Ionic Analysis of Retinal Rods by X-ray Microanalysis.

Thin Glass Film Standards for Analytical Electron Microscopy. Analytical electron microscopy is a rapidly emerging and important microanalysis technique. The purpose of this work is to develop standards for microanalysis techniques such as energy dispersive x-ray spectrometry and electron energy loss spectrometry, the two primary analytical modes of analytical electron microscopy. NBS Glass K-411 (wt. %: SiO_2, 55, FeO, 15, MgO, 15, CaO, 15) has been sputtered and 60 transmission electron microscope grids have been prepared as a candidate thin film standard for round robin analysis. The glass was sputtered onto a 20 nm carbon film carried on a standard electron microscope grid. A sputtered layer of approximately 80 nm thick was deposited. Trial grids are being distributed to four cooperating laboratories for evaluation. Preliminary work on this program will be presented at the 16th Annual Conference of the Microbeam Analysis Society, July 13-17, 1981, Vail, Colorado, in a talk by E. Steel entitled "Preparation of Thin Film Glass Standards for Analytical Electron Microscopy by Ion Beam Sputtering."

SRM 477--Glass Fluorescence Source. This 3 mm thick and 25 mm in diameter standard reference material is a glass disc used as a target source for measurement of window attenuation of semiconductor detectors in x-ray energy spectrometers in accordance with ANSI 759 of the American National Standards Institute and the corresponding standard of the International Electrotechnical Commission.

Thin Glass Film Standards for the Calibration of X-ray Fluorescence Spectrometers. Ion-sputtered glass films are promising standards for x-ray spectrometers. Previous work on this subject has been described in detail in various NBS/EPA Energy Environment Reports. A number of new glasses have been developed and seven-inch discs prepared for ion beam sputtering in continuation of this joint NBS/EPA project. Glasses for this purpose are prepared in 900-1000 gram melts and require considerable compositional adjustment to prevent crystallization on casting and cooling.

Nuclear Waste Leachability Research Materials
Subtask 5 of Task 12154

D. J. Cronin, W. K. Haller, D. A. Kauffman

As part of the NBS program in Nuclear Waste Management, the Glass Group is to develop and supply two glasses that can be used as research materials in leach testing. The need for such materials is great since in the past leaching experiments have been carried out using many different test methods and no standards. As a result it is very difficult to compare the leaching behavior of two different materials that have been tested by different methods. Standard tests are now being developed to alleviate part of the problem, but standard materials are also needed so that it is possible to assure that the tests are being run properly.

The materials supplied by the Glass Group will eventually be certified as SRM's when a suitably controlled leach test has been developed. The materials will simulate nuclear waste materials.

The development and characterization of the first research material has been completed and purchase specifications prepared. Bids on this first material will be due on October 5, 1981, so that the order can be placed early in FY82.

The development work on a second more durable material is continuing. This has involved constructing an apparatus for doing leach tests, on a weight loss basis, for the purpose of identifying promising materials. A variety of different glass compositions have been tested. This testing and development program is continuing. No decision as to the nature of the second material has been made.

In addition to producing the research materials, the Glass Group personnel also provide advice to other NBS scientists in the nuclear waste program on areas of importance involving glass. These areas include the chemical durability of glass, sample preparation, and processing of waste into glass.

Special Glass Developments
Subtask 6 of Task 12154

D. H. Blackburn, W. K. Haller, D. A. Kauffman

Laser Glasses. Work has continued in a long-standing collaboration with the Lawrence Livermore Laboratory in the field of laser research. A number of glass specimens were prepared in various glass-forming systems ranging from fluorophosphates to bismuth borates. The glasses were doped with rare earth and transition metal oxides for the study of various laser optical properties such as optical absorption and emission spectra as related to fluorescence lifetime and optical pumping efficiency.

Low Interference Intracellular Ion Selective Electrodes. A collaborative project with the National Institutes of Health has begun to develop glass-based microelectrodes to measure ion concentrations in the protoplasm of healthy and malignant cells. Present microelectrodes suffer from ion-conduction inference through the walls of the micron-sized glass capillaries and from

problems caused by the surface chemistry of the glasses. It is planned to develop sensors based on glasses without ionic conduction and to develop processes to improve the surface characteristics of the glasses.

Initial experiments were conducted to establish if fused silica tubes can be flame-drawn into capillaries of several micrometers in diameter. The experiments were encouraging and an automated drawing apparatus is presently being designed.

Resource Recovery and Utilization
Subtask 7 of Task 12154

M. J. Cellarosi

The Resource Conservation and Recovery Act of 1976 directs the NBS to provide guidelines for the development of specifications for materials recovered from wastes. The Act also instructs the NBS to cooperate with national standards setting organizations and the public on evaluation and development of necessary standards pertaining to physical/chemical properties and characteristics of recovered materials and their use in replacing virgin materials in various industrial, commercial, and governmental uses.

In the area of glass, NBS is cooperating with ASTM Committee E-38 on Resource Recovery, the glass industry, reclamation facilities, and the National Center for Resource Recovery. These activities so far have generated two standards for recovered glass specifically for reuse in container manufacturing.

Glass manufacturers use cullet (broken glass) as part of the charge to their furnaces. This long-established practice promotes the melting of raw materials and permits the reduction of furnace temperatures. Benefits of such practice translate into energy savings, extension of furnace linings life, and greater productivity. Most of the recycled cullet so far has been scrap glass from the manufacturing plant itself.

A potential new source of cullet is the glass contained in the municipal solid waste stream (about 12 percent). Several large-scale reclamation facilities have been built and others are planned. These facilities will separate the glass fraction from the other components. The glass so recovered must meet stringent standards for quality and consistency (e.g., color, contamination, etc.). Targets for reclaimed glass specifications and test methods have been set for container manufacture. Tentative standards applicable to the manufacture of glass wool insulation are currently under review.

During the year, our laboratory carried out testing of samples from initial recovery operations. Test methods cover determinations of moisture content, organic contamination, magnetic/non-magnetic contamination, color fraction, particle size, refractory content, melt evaluations, and viscosity. Results of these tests indicate that the overall quality of recovered glass has improved; however, it still falls short of meeting established acceptance standards.

NBS is continuing in coordinating and performing tests, cooperating with the National Center for Resource Recovery, EG&G, Inc., and a large glass manufacturer. Plans include large-scale production runs at a container manufacturing plant. Objective of this work is the design of second generation glass recovery

plants. Similar work is being pursued for the Hempstead Recovery Facility (New York City) with a glass plant in Dayville, Connecticut. However, operations at Hempstead are currently under suspension by EPA until guidelines on dioxin emissions are established. Cooperative efforts are in progress with Raytheon, Inc., and several glass companies for the new plant in Monroe County, Rochester, New York.

Optical Properties of Materials
Subtask 8 of Task 12154

A. Feldman, M. I. Bell, R. M. Waxler, D. H. Blackburn, M. J. Dodge, J. Malitson

Piezo-Optics. The dispersion of the piezobirefringence of two specimens of GaAs was measured over the wavelength range 3.5 μm to 10.6 μm. The specimens were prepared from single crystal slices of high resistivity (4.3×10^7 Ω cm) GaAs kindly provided by Don Hobgood of the Westinghouse Research Center. The slices were 8 cm in diameter by 1 cm thick. These slices were examined for internal strain in both an infrared polarimeter and in an infrared polarizing microscope. The information was provided to Westinghouse on a confidential basis. In turn, we prepared specimens from these slices for the piezobirefringence studies. Two specimens were prepared, one for stress along the (001) crystal axis, and the other for stress along the (011) axis. From these specimens we obtained the piezo-optic constants $q_{11}q_{12}$ and q_{44} the elasto-optic constants p_{11}-p_{12} and p_{44}, the photoelastic constants k_{11}-k_{12} and k_{44}, and the piezodielectric constants d_{11}-d_{12} and d_{44}.

The measurements were made by a variety of polarimetric techniques. A monochromator and an InSb detector were used in the range 3.5 μm to 5.4 μm; a filter wheel and a PbSnTe detector were used at 6.325 μm, 8.03 μm and 10.03 μm; a CO_2 laser, and a pyroelectric detector were used at 9.55 μm, 10.24 μm, and 10.59 μm.

Figure 1 is a plot of $k_{11}k_{12}$ and k_{44} as a function of wavelength. There is a small yet significant dispersion in the coefficients which is attributed to the stress dependence of the transverse optic phonon. The two dashed curves are the dispersions predicted by theory based on different models for the interionic potentials and the deformation dipoles. The model due to Phumphreys and Maradudin provides the better fit. The solid curve is based on a two parameter fit of the data to an oscillator model based on the strain-induced anisotropy of the transverse effective charge and the strain-induced splitting of the transverse optic phonon frequency. The phonon frequency splitting was taken from the work of Weinstein and Cardona, who measured the stress dependence of the Reststrahlen spectrum.

The results of the fit yielded the strain-induced relative anisotropies of the transverse effective charge and the high frequency photoelastic constants k_{11}^{∞}-k_{12}^{∞} and k_{44}^{∞}, which are in good agreement with extrapolations of shorter wavelength piezo-optic dispersion data. The main contribution to the observed dispersion comes from the oscillator strength anisotropy.

It should be emphasized that the data we have obtained are unique. Little infrared piezo-optic data exist and the bulk of these data are at single wavelengths. Most dispersion data are below 2.5 μm. We have been the first to obtain significant infrared piezobirefringence dispersion data beyond 2.5 μm.

Glasses for Fiber-Optic Sensors. At present there is considerable interest in the use of fiber optics for sensors of physical parameters, such as temperature, pressure, electric fields, and magnetic fields. The Navy has a particular interest in developing acoustic sensors. The Naval Research Laboratory has therefore requested that NBS aid in the development of glasses for fiber optic sensor materials and the characterization of these glasses as to elastic moduli, thermal expansion, thermo-optic constant and photoelastic constants.

The fiber-optic sensor system is conceived as being composed of two parts, the sensor itself, which is located a long distance from a monitoring station, and fiber optic leads that connect the sensor to the monitoring station. At present the emphasis of our program is on sensor lead materials, and in particular the study of materials for pressure insensitive fibers. The fiber leads are to pass through regions of the ocean that are subject to fluctuations in pressure. It is important that the optic path of propagation in the fiber core be immunized against these fluctuations in order to minimize optical noise in the sensor system. Work at NRL has shown that a cladding material with a high Young's modulus acts to minimize the effects of pressure on the fiber core. Based on past experience, we have produced thirteen glasses with Young's moduli that exceed 1.1×10^{11} N/m^2 which is well beyond the target value of 9.5×10^{10} N/m^2. Another important goal achieved was to produce this high value without the use of BeO. The elastic moduli were measured by the dynamical method of Spinner and Teft. Since cladding and core are to be fused together, the thermal expansion and viscosity relation of core to cladding glass are of utmost importance. We are now in the process of measuring the linear thermal expansion coefficients of these glasses.

As part of this study, it was of interest to determine whether cladded fibers could be drawn in which the cladding had a significantly higher thermal expansion coefficient than the core. This system is inherently unstable because the outer surface of the cladding is under tension. Douglas Blackburn, using a coating technique, has succeeded in drawing short lengths of fibers having a low expansion, high viscosity pyrex core and a high expansion, low viscosity lead silicate cladding. Although the coating technique produced bent fibers, it was surprising that the fibers did not self-destruct due to the thermal expansion mismatch which puts the surface in tension.

Refractive Index. The employee who had until recently been making precision refractive index measurements, has left the Division. The person who formerly was in charge of the refractometry laboratory, has been under contract with NBS to assess the status of the equipment, to complete any undone test work, and to conduct a survey to ascertain the need for continuation of the refractive index measurement service. The equipment assessment found that the two main spectrometers and the Abbe refractometer are in good working order, but the V-block refractometer requires repairs. Measurements of the refractive indices of two liquids for the State of New Hampshire Law Enforcement Laboratories have been completed.

An informal survey was conducted among potential users of the refractive index measurement service, and a report has been written. The general view expressed was that the service should be continued. However, requests for measurements this year have not been large. The principle inquiry came from the Raytheon Company concerning the measurement of the refractive index of a new infrared transmitting material, high purity chemical vapor deposited ZnS.

Raman Spectroscopy. Studies of ion implantation and annealing of semiconductors have continued in collaboration with R. A. Forman and D. Horowitz of the National Engineering Laboratory and D. R. Myers of Sandia Laboratories. Results on boron-10 and boron-11 implants in silicon were presented at the 1981 March meeting of the American Physical Society in Phoenix. We found, contrary to the results of others, that thermal annealing of an implanted sample under properly chosen conditions can lead to Raman spectra identical to those obtained from laser annealed samples, indicating that thermal annealing can be as effective as laser annealing in removing implantation damage. Our previous work had noted that the use of Raman scattering to assess the effectiveness of annealing in boron-implanted samples can be complicated by the coincidence of the boron-11 local mode frequency with a feature in the second-order spectrum of silicon. A comment based on this finding was published in the June 1981 issue of the Journal of Applied Physics.

A new project was begun jointly with R. Durst and K. A. Bunding of the Organic Analytical Research Division to examine surface-enhanced Raman scattering (SERS) and its potential as a tool for studying electrochemical reactions. Surface enhancement increases the Raman cross section of various molecules (e.g., pyridine) by factors of 10^6 or more when adsorbed on a suitably prepared surface of silver or certain other metals. Previous work by Dr. Bunding had shown that several derivatives of pyridine which contain carbonyl groups exhibit striking changes in their spectra when adsorbed on silver. In particular, 4-pyridinecarboxaldehyde exhibits a strong carbonyl stretching vibration in solution, but this band disappears when the molecule is on the metal surface. In an effort to explain this observation, we studied a series of pyridine derivatives: carboxaldehydes, methylketones, carbinols, and N-methyl salts. The pattern which emerged has implications both for theories of SERS and for the potential value of the effect as a tool for surface analysis. We concluded that in the molecules studied, adsorption occurs through an interaction of the metal with the nitrogen lone pair electrons, and that the effects of this interaction are transmitted through the π-electron system, producing significant changes in the electronic structure of the molecule. This charge withdrawal through the π system promotes hydration of the 4-substituted carboxaldehydes and methylketones, reducing the intensity of the carbonyl band, but has little effect on the corresponding 3-substituted compounds. Since this surface hydration occurs at potentials more positive than the reduction potential, it is clear that theories which attempt to explain SERS intensities and their potential dependence must take adsorbate-substrate interactions into account even at potentials at which no electrochemical reactions occur. A preliminary report of these results was made at the 182nd National Meeting of the American Chemical Society in New York, and a more detailed manuscript was submitted to Surface Science.

Dr. M. I. Bell has recently assumed the chairmanship of the ASTM Subcommittee E-13.08 on Raman Spectroscopy (parent Committee: E-13 on Molecular Spectroscopy). The Subcommittee is currently preparing for publication a report on a round-robin study of Raman intensities and depolarization ratios conducted several years ago with NBS support. The results of this study indicate a need for a carefully defined method for measuring depolarization ratios, and a proposal is in preparation. Another round robin will probably be undertaken to test any method which gains Subcommittee approval. Dr. Bell was invited to participate in an ASTM Symposium on "Practical Performance Testing of Spectroscopic

Instrumentation," held in conjunction with the annual meeting of the Federation of Analytical Chemistry and Spectroscopy Societies in Philadelphia, September 1981. Publication of these lectures as an ASTM monograph is planned.

Collaborations with groups at the U.S. Coast Guard Research and Development Center (Groton, Connecticut) and the University of Florence have led to arrangements for two guest workers to make use of the Raman spectroscopy facility. Mr. R. K. Kustuk of the U.S. Coast Guard has been studying the application of Raman spectroscopy to the detection and identification of hazardous chemicals in water. Data acquired at Groton have been transferred to our minicomputer, and Mr. Kostuk is developing quantitative measures of the quality of spectra and seeking to determine the detection limits for a number of common pollutants. Previous cooperation with Prof. F. Barocchi and his students at the University of Florence has continued, and M. Moraldi of that group will arrive shortly to begin an extensive study of the density and temperature dependence of Raman scattering in hydrogen.

Recent improvements in the NML Raman spectroscopy facility have included installation of a temperature-controlled circulating oil bath and capillary-tube sample holder which permit measurements over the temperature range -70 to +330 °C with a stability of 0.01 °C. Several utilities have been added to the software package for the Interdata 7/16 minicomputer which operates the spectrometer. These routines facilitate data analysis and plotting by allowing the user to scan entire spectra or selected regions to obtain maxima or minima, peak locations and heights, and average or integrated intensities. A printer and second CRT terminal have been added to the system, both of which greatly simplify program development and maintenance. Several new hardware interfaces between the minicomputer and standard microprocessor buses have been designed and are in various stages of construction and testing. These interfaces will be used to provide high-speed video graphics for interactive data analysis, to enhance the communications capabilities of the minicomputer, and to permit access to low-cost floppy disk systems.

Plans have been drawn up for a new and slightly larger laboratory to house the facility when it is relocated to the Polymers Building. The design provides for improved facilities for sample preparation, equipment maintenance, and data analysis, and for greater ease and flexibility in making special-purpose optical set-ups. Space has also been reserved for additional lasers and spectrometers so that we can continue to upgrade the facility to reflect the state-of-the-art in instrumentation for Raman spectroscopy. We expect the facility to be operational in its new location by the end of 1981.

Nondestructive Evaluation
Subtask 9 of Task 12154

A. Feldman, A. H. Kahn, G. S. White

Optical Scattering for Nondestructive Evaluation. Using the apparatus developed last year for measuring the scatter as a function of angle for 1.6 μm wavelength radiation incident upon surface grooves, data were taken of scattering from shallow rectangular and deeper V- and trapezoidal grooves.

The scalar model developed for the scattering from shallow (depth $\sim 0.05\lambda$) accurately described the observed scattering and incorporated quantitatively certain possible misalignments of the system.

Three deep V-shaped and three deep trapezoidal-shaped grooves also were obtained (figure 2) and scattering data were collected with the incident electric field both parallel and perpendicular to the groove length. The groove itself was normal to the scattering plane swept by the detector. Differences in the scattering with polarization were observed. However, the scattered fields maintained the same polarization as the incident field with no measurable cross-over.

Scalar calculations used to fit scattering from the shallow grooves were completely inadequate for describing the scattering from these deeper grooves. Daniel Maystre, a visiting French scientist from the CNRS, developed a vector theory which could be used to calculate the scattering from any cylindrical cross section due to an incident electric field polarized with E parallel to the cylinder axis.

With the help of Jay Marchiando and Ted Vorburger, in the Mechanical Production Metrology Division, the cross sections of the grooves were measured with a diamond profilometer and preliminary calculations were made for the expected scatter.

Figure 3 is a composite of scattering data measured as a function of angle for several locations along the narrow V-groove (crosses) and the calculated scatter intensity (solid line). The calculations were made by measuring the groove cross section at one position with a profilometer and calculating the scatter from that profile. The agreement between the observed and the calculated scatter intensities is excellent. Experimentally observed asymmetries are reproduced in the calculations at the correct angular positions and with proper magnitudes.

The scatter in the experimental data reflects the lack of uniformity of the groove. This lack of uniformity also causes the asymmetries observed in both the measured and the calculated scattering. The brass, during the scribing process, flows into mounds on either side of the grooves. These mounts are, in general, not symmetric and also change in height, width, and shape along the length of the grooves. Another feature contributing to the lack of symmetry in the observed scatter is that the grooves themselves are not symmetric but have one side steeper than the other. All of these effects are accounted for in the calculations.

Similar calculations have ben made for the medium sized V-groove and the narrow and medium width trapezoids with a 20 μm bottom. In these latter cases, ideally shaped grooves were incorporated into the calculations because the depths of these grooves were greater than the range of the profilometer. Nevertheless, the calculated scattering presented the same qualitative features, including number and approximate sizes and peaks, which were observed experimentally. Quantitative features, such as angular positions of the maxima and minima and observed asymmetries, are not yet in agreement with experiment. However, it has been found that these features vary significantly with relatively minor ($\sim 0.1\lambda$) changes in groove shape.

Currently, work is progressing in fitting these data more quantitatively. In the same vein, scattering from known positions on the narrow V-groove samples is being compared to that predicted based upon profilometer measurements at the same positions. Some work is also being done on the inverse problem, using calculated phases and experimentally determined amplitudes in an attempt to mathematically reconstruct surface defects.

Theoretical Modeling in Eddy Current NDE. Calculations have been performed of the eddy current distribution in the vicinity of a crack in a plane slab of conducting material. The exciting field was taken as uniform and parallel to the slab and the plane of the crack. In this analysis the crack depth was arbitrary, as was its inclination to the surface of the slab. The eddy current problem was solved by a boundary integral equation method. Calculations were performed for selected crack depths representative of all ranges of the ratio of crack depth to electromagnetic skin depth, and for a variety of crack inclinations. The total impedance change produced by a perpendicular crack is shown in the accompanying figure 4. These results are being used in the development of microwave crack detection equipment.

Solid State Transport
Subtask 10 of Task 12154

C. K. Chiang, A. D. Franklin, A. L. Dragoo

Major emphasis during the past year has been on the development and application of impedance spectroscopy as a measurement technique for studying solid, non-metallic electrical conductors.

The frequency dependence of the impedance of the system Electrode/Solid Electrolyte/Electrode contains information about charge transport processes not only at the solid electrolyte/electrode interfaces and within the single-crystal grains of the solid electrolyte itself, but also at the internal interfaces within the electrolyte. For a ceramic material, the electrolyte/electrode-effect impedance is observed at low frequencies and high temperatures, and the intrinsic lattice impedance is observed at high frequencies and low temperatures. The impedance due to the effects of internal inhomogeneities is found at intermediate frequencies and temperatures. These inhomogeneities include large imperfections, pores, precipitates, second phases and grain boundaries. AC impedance data for Y-doped CeO_2, Mg-doped and Y-doped ZrO_2 ceramics and its bi-crystals, Sr-doped $LaCrO_3$, and Ca-doped $YCrO_3$ have been obtained and used to illustrate these effects.

The impedance of a single grain boundary in Y-stabilized ZrO_2 has been isolated by this technique. The measurements are shown in figure 1a, in the form of the complex-plane plot of the imaginary part (Z") of the impedance against the real part (Z'), with a frequency parameter increasing from right to left. The bicrystal data repeats the single crystal data plus an additional contribution, shown in figure 1b, arising from the grain boundary alone. These latter data in turn can be analyzed in terms of the resistance and capacitance of the grain boundary itself, and thus can be used to study these properties as the grain boundary structure and composition is varied. A manuscript on this study is in preparation.

This use of the technique to study grain boundaries is not limited to such simple geometries as the bicrystal. Much the same sort of data are found with polycrystalline materials. We have completed such a study on Y-doped CeO_2, and have a manuscript in preparation. However, it is not clear how such data are to be interpreted. The first problem is the choice of an equivalent circuit, including how to incorporate a distribution of grain and grain boundary properties, and the second is how to derive the equivalent circuit parameters from the data.

A widely invoked equivalent circuit consists of a series arrangement of parallel RC circuits, each corresponding to a contribution to the impedance (grain interiors, grain boundaries, Faradaic reaction at the electrodes, etc.). For such a circuit we have developed a numerical Fourier transform technique that allows us to derive the form of the distribution of time constants from the data instead of having to assume it. This work, carried out while one of us (A. D. Franklin) was on assignment at Flinders University in Adelaide, Austrlia, in collaboration with Professor H. J. deBruin there, is almost completed and a manuscript is in preparation.

We are studying the application of the effective medium theory to the problem of the impedance of a polycrystalline material with a distribution of properties. In the absence of such a distribution the model leads rather simply to several equivalent circuits appropriate for use with impedance data. However, the situation is much more complex in presence of a distribution, and the problem is to determine under what conditions an equivalent circuit that is convenient from the standpoint of data analysis may be an appropriate physical representation of the sample.

Several material studies are in progress using the impedance technique. Matter transport in nuclear waste material is undesirable, and candidate materials may be screened using impedance measurements. Furthermore, the spectroscopic nature of the technique may allow some insight into the nature of the barriers to matter transport, as a guide to material development. We have performed such measurements on several hollantite-type materials, namely, $Ba_xAl_{2x}Ti_{8-2x}O_{16}$, $x = 1.23$ and $Ba_xMg_xTi_{8-x}O_{16}$, $x = 1.33$, both pure and with 10 percent of the Ba replaced by Cs and K. Interpretation of these data are still proceeding.

Fluorite-structure oxides containing aliovalent cations have a tendency to exhibit some ordering among those cations, thereby suffering some increase in resistivity. This is one mechanism thought to produce an "aging" effect in the resistance of solid electrolytes composed of these materials. We have embarked on a more detailed study of the aging in Y-doped CeO_2. To date, a series of anneals have been completed at 1000 °C on specimens containing 10 and 30 cation percent Y. Figure 2 displays, as a function of annealing time, the separate lattice and grain boundary resistances of the 10 percent composition, and demonstrates that at this temperature, composition, and time span the aging is solely in the grain boundary resistance, and cannot be attributed to the onset of cation ordering in the lattice.

A. D. Franklin spent an approximately five-month period (10 November 1980 to 24 March 1981) in Australia as part of the U.S./Australia Science Exchange Program under the auspices of the National Science Foundation.

The bulk of the time was spent at Flinders University, Adelaide, as discussed above, but some time was also spent at the National Measurement Laboratory in Sydney, studying point defect relaxation and transport phenomena in ionic crystals, and at the Physics Department of the Faculty of Science of the Australian National University in Canberra, studying the dating of sediments by thermoluminescence.

Electrocatalysis
Subtask 11 of Task 12154

M. I. Cohen

These efforts are directed at the need for measurement of the electrochemical characteristics of materials. The primary effort is toward the development of automated instrumentation for both laboratory and field acquisition of data to be used for the determination of these characteristics. This program is being funded by other agencies (DOT and EPRI). Although each agency has a particular objective, the two are complementary, enabling a single comprehensive design for instrument construction.

The programs consist of:

1. Federal Highway Administration--Measurement of Corrosion of Reinforcing Bars in Concrete

2. Electric Power Research Institute--Corrosion of Concentric Neutral Cable for Power Distribution

These programs are joint efforts of Division 565 with the Chemical Stability and Corrosion Division (561), and they will be discussed as a unit.

The instruments being developed are a direct outgrowth of one designed previously for use with a program in electrocatalysis for fuel cells. The design has been upgraded by going to a higher performance processor (6809). This change enables an improvement in speed and flexibility with minimal effects on the hardware. This original unit, as modified, is serving not only as an operating device, but as a development system for the other systems being built. Two are under construction, one a laboratory system and the other a field unit.

The field unit is a smaller version of the lab system and is intended as a prototype. Upon final acceptance by the agencies, it will be adapted to weather extremes and then duplicated and issued to various operational units.

The laboratory system is capable not only of operation identical to that of the field unit, but can also perform other more complex operations. Software is interchangeable between the two versions. Since the hardware in each is identical, new techniques can be tested on the lab system and when perfected, transferred to the field unit.

The primary technique used at the moment in these instruments is a variation of that used in the original instrument. The interfacing to the measurement board is the same, but we are doing a galvanostatic determination instead of a potentiostatic. In this technique, we measure the potential difference between

the working electrode and a reference electrode due to a current impressed between the working electrode and the counter electrode. By suitable timing choices, the corrosion potential can be measured (when the polarizing current is off) at the appropriate point on the waveform to eliminate the effects of the resistivity of the surrounding electrolyte (concrete or soil depending upon which of the other programs is involved).

Instrumentation Services (M. I. Cohen). The advisory, consultive and educational activities we have been providing have expanded to the limit of the personnel available pursuant to requirements of other activities. Included in this expansion have been several interface design and construction projects within the Center. A few examples are:

1. An interface unit to incorporate a digital thermometer readout into the real-time image on a video display system associated with a high temperature microscope.

2. Design and develop a small microprocessor based system (less than 10 integrated circuits) to interface with an Interdata minicomputer for bootstrapping and communication purposes.

3. Design and construction of an Interface between an MC 6800 based microcomputer system and some S-100 bus based peripherals (with M. I. Bell).

Electrical Conductivity and Polarization in Coal Slag (W. R. Hosler). In several emerging energy technologies, high temperature materials play a basic function in the performance of the system. One of these systems is MHD (magneto-hydrodynamics) where the wall temperature of the MHD duct can reach temperatures as high as 1800 °C. The walls are necessarily composed of electrode and insulator materials which must withstand these high temperatures. Furthermore, current densities on the order of 1 to 2 A/cm^2 must pass through the electrode materials ($\perp$ to channel wall) while the insulators must inhibit the flow of current in the direction of the plasma flow ($\parallel$ to channel wall). The U.S. effort in MHD is pointed toward using the direct combustion of coal to generate the hot plasma in a functioning generator. Coal slag (non-combustible residue) will deposit on the channel walls and this too will be subjected to the current transport from the plasma through the electrodes to the lead out materials. It then becomes necessary to fully understand the transport mechanisms in slag in order to design a duct wall properly and to manage the electrochemical effects which result from the high temperatures and large currents involved in a functioning generator. The conductivity in coal slag is complex depending on the slag composition and the temperature at which the slag is maintained. Recent studies have been carried out on a typical Western slag derived from coal originating from the Rosebud seam in Montana. This slag is relatively low in iron (3 to 4 percent) and high in calcium (10 to 15 percent) compared to a typical Eastern slag. Measurements were made using a 4 probe dc and ac method described in detail in quarterly reports to DOE over the past year.

One of the purposes of the electrical measurements and analysis is to try to correlate the electrical conductivity with a component in the sample at a particular temperature. One way to do this would be to quench each sample very rapidly to low temperature just after the electrical measurement

at an elevated temperature and then make a possible correlation between conductivity and component materials and physical state. This would be a very time consuming process requiring attachment of the platinum electrodes through the alumina crucible walls thus constructing a new cell for each temperature point. A certain time is required at every temperature for the conductivity to become stabilized. This time temperature relationship was obtained during the course of the regular conductivity experiments. A furnace was so arranged that samples of slag in alumina crucibles identical to conductivity samples but without the probes could be dropped into a water bath. The furnace was programmed to hold a set temperature for the time determined for stabilization after which a sample was quenched; the programmed temperature dropped to another set temperature for a specified time, another sample quenched and so on. A series of quenched samples were prepared in this manner. Those samples quenched from temperatures above 1350 °C showed only a small amount of crystalline material composed of Al_2O_3 and SiO_2 (near sillimanite) when analyzed by XRD spectroscopy. Below this temperature to 1070 °C, no crystalline phases were detectible. At 1025 °C and below the XRD pattern was strong in anorthite ($CaAl_2Si_2O_8$) or potash feldspar (KAl_2O_4) and leucite ($KAlSi_2O_4$) with a small amount of hercynite ($FeAl_2O_4$).

EDX analysis showed areas that appeared to have a crystalline nature. Lighter areas always had Fe, Al and Mg combinations which suggest an magnesia-iron alumina spinel. In these areas generally Ti and Ca were present. Other areas showed Al, Si, K and Ca combinations.

Of all these materials only the hercynite and the iron magnesia alumina spinel would exhibit appreciable conductivity. Since no crystalline components were detected at temperatures of 1070 °C and above, the conductivity must be due to components of the slag in an amorphous state. Above 1400 °C, it has been demonstrated that the conductivity is affected by the movement of iron ions. Below 1400 °C the contribution of these ions is not known and the conductivity mechanism is still in doubt.

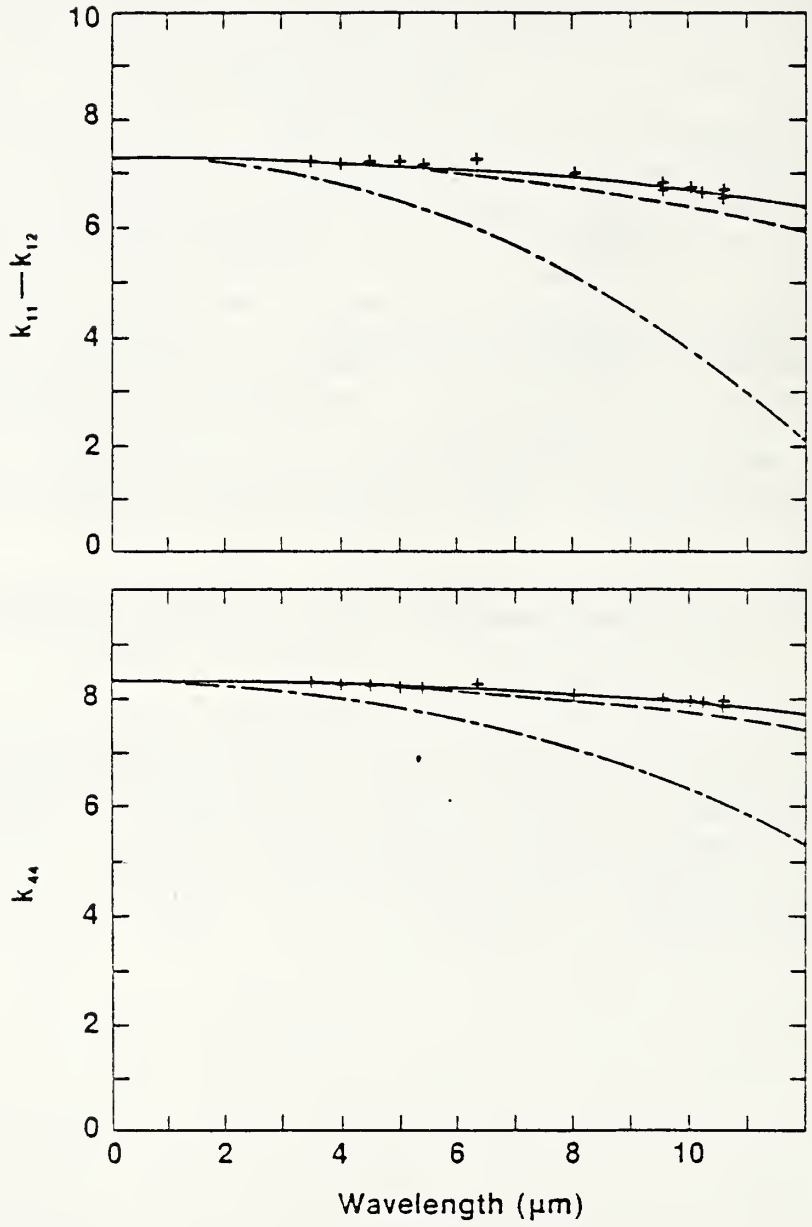


Figure 1. Photoelastic constants k_{11}-k_{12} and k_{44} of GaAs. The pluses are the experimental data points. The solid curve is a two parameter fit. The short dashed line is from the theory of Humphreys and Maradudin. The long dashed line is from the theory of Bendow, Gianino, Tsay, and Mitra.

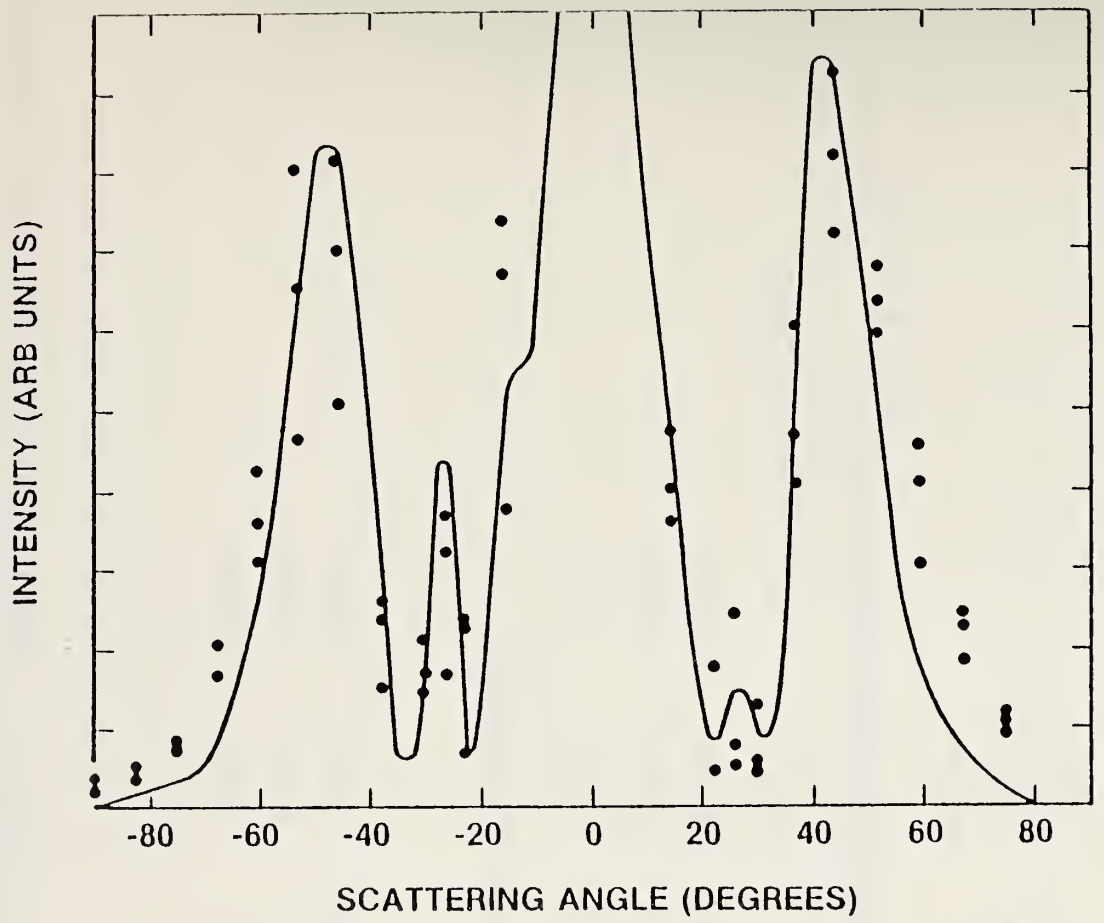
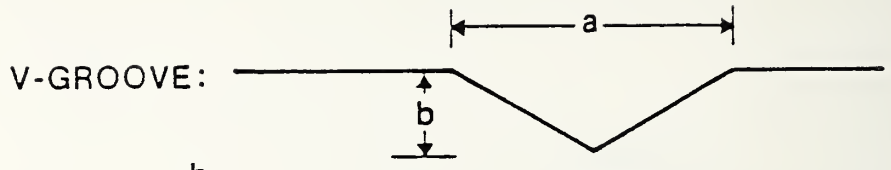
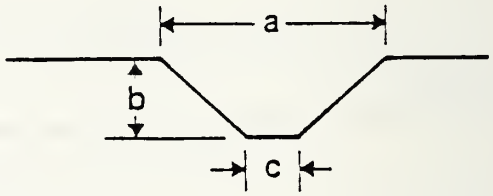


Figure 2. Composite of experimental and theoretical scattering from narrow V-groove. Solid curve was calculated from one profilometer cross section measurement of the groove. The points (*,+,x) are experimental data obtained from three different positions on the groove.



V-GROOVE:

a	b
34 µm	8.4 µm
90.7 µm	17 µm
122 µm	43 µm



NARROW TRAPEZOID:

a	b	c
64 µm	21 µm	20 µm
79 µm	27 µm	21 µm
152 µm	77 µm	21 µm

WIDE TRAPEZOID:

a	b	c
89 µm	15 µm	51 µm
128 µm	57 µm	51 µm
148 µm	69 µm	51 µm

Figure 3. Cross sections and nominal dimensions of ideal deep V-grooves and trapezoids.

Other Activities of the Ceramics, Glass, and Solid State Science Division

Invited Talks

Glass Vaporization Work at NBS
IBM, Yorktown Heights, New York
D. M. Sanders
August 19, 1980

Characterization of Power Plant Ash with Emphasis on RDF
ASME Research Committee on Industrial and Municipal Wastes
National Bureau of Standards, Washington, D.C.
C. R. Robbins
September 1980

The Properties and Performance of Materials in the Coal Gasification Environment
GRI/MPC/ASM/DOE Conference, Pittsburgh, Pennsylvania
S. M. Wiederhorn, E. R. Fuller, Jr., and C. R. Robbins
September 1980

Transport Properties of Polycrystalline Ceramics from Impedance Measurements
New England Section, American Ceramic Society, Boston, Massachusetts
A. D. Franklin
September 18, 1980

Glass as a Material for Asbestos Standards
NBS/EPA Workshop on Asbestos Standards, Gaithersburg, Maryland
D. J. Cronin, D. H. Blackburn, and W. K. Haller
October 3, 1980

Viscosity of Glasses in the System CaO-MgO-Al_2O_3-SiO_2
Fall Meeting, Glass Division, American Ceramic Society, Bedford Springs, Pennsylvania
D. J. Cronin and J. T. Wenzel
October 10, 1980

Preparation and Characterization of Amorphous Thin Films by Co-evaporization
27th National Vacuum Symposium and Vacuum Show, Detroit, Michigan
D. M. Sanders, E. N. Farabaugh, W. S. Hurst, and W. K. Haller
October 13-17, 1980

Reference Intensity Ratios in Quantitative Analysis
Pittsburgh Diffraction Conference, Pittsburgh, Pennsylvania
C. R. Hubbard
October 1980

Reliability of Particle Structure Factors Determined by Anomalous Dispersion of X-rays
Washington Crystal Colloquium, Geophysical Laboratory, Washington, D.C.
R. G. Munro
October 1980

Fluidic Temperature Sensors: Design, Processing, and Materials
Proceedings 20th ASME Annual Conference, Chicago, Illinois
T. Negas
November 1980

Phase and Microstructure Analyses
Workshop on Analytical Methodology for Nuclear Waste Disposal, Seattle, Washington
R. S. Roth
November 1980

Raman Spectroscopy: Principles and Applications
U.S. Food and Drug Administration, Division of Drug Chemistry, Washington, D.C.
M. I. Bell
November 6, 1980

Impedance Spectroscopy
National Measurement Laboratory, Sydney, Australia
A. D. Franklin
November 16, 1980

Recent Developments in Fuel Cell and Related Materials Research
National Measurement Laboratory, Sydney, Australia
A. D. Franklin
November 21, 1980

Relaxation Modes in Dielectric Phenomena
National Measurement Laboratory, Sydney, Australia
A. D. Franklin
November 26, 1980

Optical Properties of Thin Films
Division Seminar, Ceramics, Glass, and Solid State Science Division, National Bureau of Standards, Washington, D.C.
A. Feldman
February 1981

Impedance Spectroscopy
C.S.I.R.O. Division o Materials Science, Melbourne, Australia
A. D. Franklin
February 16, 1981

Fuel Cell R&D in the United States
C.S.I.R.O. Division of Mineral Chemistry, Melbourne, Australia
A. D. Franklin
February 17, 1981

Impedance Spectroscopy
Department of Physics, Australian National University, Canberra, Australia
A. D. Franklin
March 17, 1981

Fourier Transform Technique for Deriving Distribution of Time Constants from Impedance Data
National Measurement Laboratory, Sydney, Australia
A. D. Franklin
March 23, 1981

Arc Plasma Spray Coatings for Fluidic Pyrometer Sensors
International Conference on Metal Coatings, San Francisco, California
T. Negas and D. H. Harris
April 7, 1981

Symposium on Automation in OSRD Data Centers (NBS), Numerical I, File Design and Information Content
National Bureau of Standards, Washington, D.C.
A. D. Mighell and J. K. Stalick
May 1981

Standards for X-ray Powder Diffraction
State University of New York at Albany, New York
C. R. Hubbard
June 1981

Fluidic Capillary Pyrometer and Fluidic Gas Concentration Sensor
1981 Symposium on Instrumentation and Control of Fossil Energy Processes, San Francisco, California
R. M. Phillippi and T. Negas
June 9, 1981

Phase Equilibria, Crystal Chemistry of the Systems $BaO-Nd_2O_3-TiO_2$, $BaO-Al_2O_3-TiO_2$, and $BaO-MgO-TiO_2$
Josef Stefan Institute, Ljubljana, Yugoslavia
R. S. Roth
June 25, 1981

High Pressure Studies of CdS
Rensalerville, New York
S. Block and G. J. Piermarini
June 1981

The NBS/DOE Materials Components Performance and Properties Data Bases
Department of Energy, Morgantown, West Virginia
H. M. Ondik
July 1981

Ternary Non-stoichiometric Phases in the System $BaO-Al_2O_3-TiO_2$, $BaO-MgO-TiO_2$, $Cs_2O-MgO-TiO_2$, $Cs_2O-Al_2O_3O-TiO_2$, and Their Relationship to Nuclear Waste Encapsulation
CNRS Seminar, Laboratoire de Cristallographie, Grenoble, France
R. S. Roth
July 9, 1981

Low Z Glass Standards for Biological X-ray Microanalysis
16th Annual Conference of Microbeam Analysis Society, Vail, Colorado
C. Fiori and D. H. Blackburn
July 13-17, 1981

Crystalline Alternates to Glass for Nuclear Waste Encapsulation
Josef Stefan Institute, Ljubljana, Yugoslavia
R. S. Roth
July 13, 1981

Crystal Growth Techniques at the National Bureau of Standards
Josef Stefan Institute, Ljubljana, Yugoslavia
R. S. Roth
July 13, 1981

The NBS Crystal Data File
IUCr Symposium on Data Bases and Data Centers, Ottawa, Canada
A. D. Mighell and J. K. Stalick
August 1981

Impedance Changes Produced by a Crack in a Plane Surface
DARPA/AF Review of Progress in Quantitative NDE, Boulder, Colorado
A. H. Kahn
August 4, 1981

Sintering in the System Mullite-Leucite-Anorthite
5th International Round Table Conference on Sintering, Portoroz, Yugoslavia
L. P. Cook and S. Pejovnik
September 7, 1981

Practical Performance Testing of Instrumentation for Raman Spectroscopy
Federation of Analytical Chemistry and Spectroscopy Societies Meeting,
Philadelphia, Pennsylvania
M. I. Bell
September 20, 1981

Technical and Professional Committee Memberships

American Ceramic Society
- Committee on Publications
  - Subcommittee on "Phase Diagrams for Ceramists"
  - R. S. Roth, Chairman

American National Standards Institute
- S. Block, Member: N43
  - Chairman: N43.1
- M. J. Cellarosi, Member: F1-Hybrid Electronics
- D. J. Cronin, Member: Z26.1-Safety Glazing of Motor Vehicles
  - Z97-Architectural Safety Glazing

American National Standards Institute
- F. A. Mauer, Secretary: N43.01

American Society for Testing and Materials
- W. S. Brower, Member: C8-Refractories
- C. R. Robbins, Member: C9-Concrete and Concrete Aggregates
- M. J. Cellarosi, Vice Chairman: C14-Glass and Glass Products
  - Member: C14.01-Nomenclature of Glass and Glass Products
  - C14.04-Physical and Mechanical Properties of Glass
  - C14.08-Flat Glass
- W. K. Haller, Member: C14.03-Chemical Properties of Glass
- D. J. Cronin, Member: C14.04-Physical and Mechanical Properties of Glass
- C. R. Robbins, Member: C18-Natural Building Stones
  - C18.0304-Sandstone
- M. I. Bell, Member: E13-Molecular Spectroscopy
  - E13.03-Infrared Spectroscopy
  - E13.08-Raman Spectroscopy
  - E13.90-Executive Subcommittee
- M. J. Cellarosi, Member: E38-Resource Recovery
- C. R. Robbins, Member: E38-Resource Recovery
- M. J. Cellarosi, Member: E44-Solar Heating and Cooling
- A. Feldman, Member: F1.02-Laser

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- A. D. Mighell, Liaison Officer

CRC Handbook Series in Laser Science and Technology
- Advisory Board
  - A. Feldman, Member

Data Commission of the International Union of Crystallography
- A. D. Mighell, Member

Electronic Industries Association
- Committee on X-ray and Implosion TV Standards
  - M. J. Cellarosi, Member

Greater Washington Solid State Physics Colloquium
Steering Committee
M. I. Bell, Treasurer
Member, Executive Committee

International Commission on Glass
W. K. Haller, U. S. Representative
Member, Subcommittee A,II: Durability and Analysis
Vice Chairman, Subcommittee VIII: Standard Reference Glasses

JCPDS-International Centre for Diffraction Data
S. Block, Member
C. R. Hubbard, Member: Board of Directors
Technical Committee
Long-range Planning Cmmittee
Ceramics Subcommittee
Data Collection and Analysis Subcommittee
Data Base Subcommittee
Search/Match Methods Subcommittee

Joint Electron Devices Engineering Councils
X-ray and Implosion TV Standards Committee
M. J. Cellarosi, Member

PDF Data Base Task Group
J. K. Stalick, Member

Washington Editorial Review Board
A. Perloff, Member

Publications

Thermal Stability of Long-range Order in Oxides
R. S. Roth
Progress in Solid State Chemistry 13, 159 (1980)

Lead Alkali Apatites Without Hexad Anion: The Crystal Structure of $Pb_8K_2(PO_4)_6$
M. Mathew, W. E. Brown, M. Austin, and T. Negas
J. Solid State Chem. 35, 69 (1980)

Neutron Powder Diffraction Study of the Structures of $CeTaO_4$, $CeNbO_4$, and $NdTaO_4$
A. Santoro, M. Marezio, R. S. Roth, and D. B. Minor
J. Solid State Chem. 35, 167 (1980)

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R. G. Munro
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The Effect of Striae on the Strength of Glass
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Vaporization in an Unstirred Soda-Lime-Silica Glass Melt
S. Murai, J. T. Wenzel, and D. M. Sanders
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Piezo-optic Coefficients of Four Neodymium Doped Laser Glasses
R. M. Waxler and A. Feldman
Appl. Optics 19, 2481 (1980)

Effects of Stress on the Raman-active Modes in Semiconductors
M. I. Bell
Proc. VII Int. Conf. on Raman Spectros., W. F. Murphy, ed. (North Holland, Amsterdam, 1980), p. 76

Effects of Inhomogeneous Strain in Ferroelectric Crystals Near Their Phase Transitions
G. M. Loiacono, M. Delfino, A. Shaulov, W. A. Smith, and M. I. Bell
Ferroelectrics 29, 81 (1980)

Viscosities and Glass Transitions in Liquids at High Pressures
R. G. Munro, G. J. Piermarini, and S. Block
Rev. Phys. Chem. Japan, The Review of Physical Chemistry of Japan
50th Commemorative Volume (1980)

Transport Properties by Impedance Measurements for Solid Electrolyte-fuel Cells
J. R. Bethin, C. K. Chiang, A. L. Dragoo, and A. D. Franklin
Proc. Nat. Fuel Cell Seminar, July 14-16, 1980

An Assessment of Open Cycle Magnetohydrodynamics (MHD) Technology
S. J. Schneider, T. Negas, W. R. Hosler, and J. D. McKinley
Prepared for National Science Foundation (August 1980)

Standard X-ray Diffraction Powder Pattern, Section 17, Data for 54 Substances
M. C. Morris, H. F. McMurdie, E. H. Evans, B. Paretzkin, S. J. Carmel, and C. R. Hubbard
NBS Monograph 25, Section 17 (October 1980)

Optical Nondestructive Evaluation
A. Feldman and G. White
NBS Dimensions (November 1980)

Refinement of the Structure of Solid Methane
S. F. Trevino, E. Prince, and C. R. Hubbard
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R. A. Forman, D. R. Myers, M. I. Bell, and D. Horowitz
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Effects of Adsorption on Electronic Structure: SERS of Pyridinecarboxaldehydes and Methyl Ketones on Ag Electrodes
K. A. Bunding and M. I. Bell
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An Impedance Spectroscopy Model for Electron Transfer Reactions at an Electrode/Solid Electrolyte Interface
H. J. deBruin and A. D. Franklin
J. Electroanal. Chem. 118, 405 (1981)

An Oxygen-sensitive Electrode Impedance in Sr-doped $LaCrO_3$
J. Bethin, C. K. Chiang, and A. D. Franklin
J. Appl. Phys. 52 (1981)

A Boundary Integral Equation Method for Calculating the Eddy Current Distribution in a Long Cylindrical Bar with a Crack; Eddy Current Characterization of Materials and Structures
A. H. Kahn and R. Spal
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The Application of a General Equation for Controlled Pore Glass Permeation Chromatography to an Aggregating Spherical Virus
W. Haller, H. H. Gschwender, K.-R. Peters
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Nancy M. O'Fallon
Argonne National Laboratory
September 11, 1980

"Diffusion Phenomena in Silicate Glasses"
H. A. Schaeffer
University of Erlangen, Nünberg, Germany
October 6, 1980

"CHESS: A New High Energy Synchrotron Radiation Source at Cornell"
Cornell University, B. W. Batterman
October 17, 1980

"Central Force Network Dynamics in Glasses: Raman, I.R., and Neutron Studies"
F. Galeener
Xerox Corporation
October 31, 1980

"Internal Boundary Layer Phenomena in Dielectric Ceramics"
David A. Payne
University of Illinois
November 20, 1980

"Intervalence Transitions in Mixed-Valence Minerals of Fe and Ti; Exciting Times for Electrons in Gems and Minerals"
R. G. Burns
Massachusetts Institute of Technology
December 2, 1980

"Stresses in Glass-to-Metal Seals"
Arun K. Varshneya
General Electric Lighting Business Group
December 15, 1980

"Recent High Pressure Researches at Nagoya University--Solid Solubility of Aluminum Alloys, P-V Relations of Metals"
Ikuya Fujishiro
Nagoya University, Japan
January 29, 1981

"Optical Properties of Thin Films"
Albert Feldman
National Bureau of Standards, Gaithersburg, Maryland
February 24, 1981

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Anna E. McHale
Massachusetts Institute of Technology
May 11, 1981

"Microstructural Aspects of Fast-Ion Conduction in Solids"
J. Drennan
Imperial College of Science and Technology, Royal School of Mines, London
May 26, 1981

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A. D. Franklin
National Bureau of Standards, Gaithersburg, Maryland
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March 1981, pending

REACTOR RADIATION DIVISION

REACTOR RADIATION DIVISION (566)

Robert S. Carter, Chief
Tawfik M. Raby, Deputy Chief
E. C. Maxwell, Administrative Officer
L. L. Sprecher, Secretary
T. L. Mangum, Secretary

The NBS Reactor is a national center for the application of reactor radiation to a variety of problems of national concern. The major areas of activity are:

Materials Characterization
Nondestructive Evaluation
Trace Analysis
Radiation Standards and Measurement

The Reactor Radiation Division (RRD), in collaboration with other scientists within CMS, other NBS Centers, and outside organizations, uses neutron scattering methods to determine the properties and behavior of materials at the atomic level. These methods are used to study a wide variety of problems such as hydrogen in metals, the microstructure of rapidly solidified materials, microscopic properties of advanced crystalline and amorphous magnetic materials, polymers, molecular species and interactions on catalytic surfaces, and the structure of biological molecules. These measurements contribute to an understanding of hydrogen embrittlement of metals, alloys and magnetic materials, ceramics and fast-ion conductors, polymeric structure, chemical catalysis, and biological processes. NBS is in a unique position to carry out such a multidisciplinary program because of its strong materials programs centered in CMS and other Centers and its unique reactor facilities that are not available in industrial laboratories.

In the area of nondestructive evaluation, RRD uses neutron radiography and both large and small-angle neutron diffraction to examine objects for defects or hidden components that must be examined nondestructively. The major effort is in developing improved methods and standards. Standards are needed for the characterization of industrial neutron radiography facilities. Improved methods range from radiographic image enhancement systems to the use of small-angle neutron scattering (SANS). Applications include such diverse uses as the autoradiography of rare paintings to verify their authenticity and the use of neutron scattering to determine the distribution of defects in structural material. This program is partially funded through the Office of Nondestructive Evaluation and is part of the Bureau-wide effort to improve productivity through better quality assurance and increased component lifetime.

Neutron activation analysis is a very sensitive technique for measuring trace elements at very low concentrations. RRD provides the sample irradiations, but the program and sample analysis are carried out by the Center for Analytical Chemistry. It is used extensively for characterizing Standard Reference Materials and a variety of other measurements such as the determination of impurities in solar cell materials and environmental studies. A large number of outside organizations also use this technique for measuring trace elements

or pollutants in foods and drugs, environmental samples, criminal artifacts, etc. This is one of the largest neutron activation analysis activities in the country with many thousands of samples irradiated each year.

The program in radiation standards and measurements is carried out by the Center for Radiation Research. Through the use of double fission chambers and a series of accurately calibrated fission foils, they provide the basis for reactor neutron flux and power density measurements needed in the U.S. fast-flux development program. The calibration and intercomparison of the series of fission foils makes use of standard reference neutron fields established in the thermal column of the NBSR. CRR also maintains well characterized, filtered neutron beams in the reactor of 2 keV, 25 keV, and 144 keV energy for the calibration and development of personnel neutron dosimeters.

A number of other programs within and outside NBS utilize the long-term irradiation facilities at the NBSR for activities ranging from γ-ray and x-ray physics and standards to applications of isotopes in medical diagnosis.

As is indicated above, RRD has a duel function. It conducts research programs in the areas of materials characterization and NDE and serves as a focal point of neutron scattering expertise for many other programs within and without the Bureau. The second function includes not only the operation of the reactor, but also providing sample irradiation services for a large number of users.

An important part of the overall Reactor Division contribution to the NBS mission and to the scientific and technical community is in fostering the utilization of the reactor by other NBS groups and outside organizations. Interactions with other scientists and organizations take the form of both collaborative efforts and independent programs which rely on utilization of the reactor and facilities provided by the NBSR staff. The extent of such interactions for FY81 are indicated in the tables below. The number of personnel shown in tables 1 and 2 include many short-term collaborators as well as permanent other agency and university guest workers. These numbers are constantly changing and so may not be exact.

Collaborative interactions are those in which workers from outside the RRD collaborate scientifically with RRD scientists on problems of mutual interest. These interactions are summarized in table 1.

Table 1. Collaborative Interactions

	No. of Personnel FY81
RRD Permanent Scientists	12
Non-RRD Participants	
Other NBS	20
Other Agency	31
University	30
Industrial	9
Total Non-RRD	90

Table 2. Independent Programs

	No. of Personnel FY81
Other NBS	33
Other Agencies	22
Universities	20
Industrial	5
Total	80

Independent programs are those programs carried out independently of the Reactor Radiation Division scientific staff by other NBS Divisions and outside organizations. Table 2 summarizes these interactions.

These tables demonstrate the extensive utilization of the NBS reactor by scientists and engineers from outside the Division. They come from 18 NBS Divisions and offices, 20 Federal agencies and national laboratories, and more than 25 universities and industrial laboratories.

Many of the other agency and university collaborators have worked with us regularly for many years. Five of them (two from the Navy and three from the Army) are assigned to work full time at the reactor on a permanent basis. Others regularly spend two or three days a week at the reactor. Bureau collaborative programs include measurements on ionic crystals, polymers, simple liquids, surface molecules, hydrogen embrittlement, etc. Major independent (non-collaborative) Bureau programs include trace analysis by a neutron activation analysis, standard neutron fields for neutron flux calibration and materials dosimetry, and precision gamma-ray energy measurement.

The modernization of the secondary cooling system is completed. All the modifications to the secondary piping have been made. The new cooling tower has been hooked up and the reactor is now operating on the new upgraded secondary system.

The application for the renewal and amendment to the reactor license for 20 MW operation was submitted in December 1980. The NRC accepted our application and on December 24, 1980, they published in the Federal Register their intent to consider our application and provided the opportunity for members of the general public to intervene in the procedure. No one intervened. Although there were no intervenors, the consideration of our application has been made more complicated by the NRC's legal staff decision that a full fledged Environmental Impact Statement must be prepared. This has delayed the review process, but we still hope to receive a license early next year. Once we receive our license, the minor modifications to the primary cooling system can be completed and the testing necessary for 20 MW started. We should be at 20 MW about three months after we receive our license.

We have received our last fuel elements from our present supplier, Texas Instruments. As mentioned in last year's report, they are going out of business. The Department of Energy through the Oak Ridge Operations Office sent a "Request for Proposal" (RFP) to all potential fabricators. The response was somewhat

better than anticipated, and they have now negotiated a contract with the new supplier, Babcox and Wilcox. We should be receiving fuel from them shortly before our present reserve runs out.

The independent programs were outlined earlier in this section. Since RRD does not have any direct input into these programs, they will not be discussed further here. They are included in the reactor annual report "NBS Reactor: Summary of Activities." Preliminary copies of this summary for July 1980 to June 1981 will be made available to Panel members prior to the meeting.

The scientific work of the Reactor Radiation Division and its collaborators are summarized later in this report and details are given in the "Summary of Activities" mentioned above. A few highlights will be given here to indicate the current direction and accomplishment of the Division.

During the past year, the first major task of our Division's competence initiative in Advanced Neutron Methods has been completed. The NBS Small-Angle Neutron Scattering Facility has been installed and tested. The first extensive measurements on the facility (on polymer structure) have been completed by Charles Han, et al. of the Polymer Division, using the 25 cm x 25 cm area detector. The first results have clearly demonstrated the state-of-the-art capability of the new facility. A number of cooperative research efforts have been initiated which will utilize our SANS and other neutron diffraction facilities, including e.g., efforts with Divisions 562 and 564, and Navy labs on microcracks and phase precipitations in ceramics and metals, and rapidly solidified alloys; research on the structure of polymers, zeolytes, and metal-metalloid compounds with Union Carbide, Exxon, and Allied Chemical scientists; and studies of clustering and critical phenomena with the University of Maryland. Our attempt to hire a third new scientist under the competence initiative has been delayed by the slot freezes and reduction-in-force action at NBS over the past year.

Major accomplishments in our other research and measurement tasks include the in situ investigation of hydrogen in metals at the 10 ppm level by neutron vibrational spectroscopy. Utilizing similar techniques, we have also directly probed the local potential of hydrogen trapped by both interstitial and substitutional defects in niobium, measured tritium vibrations in a metal for the first time, and investigated the interactions of CO and H coexisting on a catalytic surface. In addition, we have used high resolution neutron diffraction and spectroscopy information on the structure and atomic transport mechanisms in a number of prototype materials for high temperature batteries, pacemakers, and electronic ceramics. This extensive work involved a variety of cooperative research interactions with other CMS Divisions, and guest workers from industrial labs (Bell Labs, Medtronics), Argonne, MIT, University of Grenoble, etc. In the area of improved measurement methods, our crystallographic staff has successfully utilized recently developed NBS improvements in profile refinement procedures to solve the structures of several intercalation compounds and have developed a new statistical test to provide enhanced ability to decide between two very similar structures in crystallographic analysis. In the NBS-NIH program on the structure of biological material, our scientists have utilized a novel method for enhancing signal-to- noise ratios in diffraction data from position-sensitive detectors and other improved refinement procedures to solve the structure of the protein (enzyme) ribo-

nuclease A to 2Å resolution from neutron and x-ray data. Finally, the principal scientist of our subtask on Magnetic and Amorphous Materials was one of the leaders of the joint Metallurgy-Reactor competence initiative on the Science of Nonequilibrium Materials, which is one of seven NML initiatives considered for FY82 funding by the NBS Director.

Plans for the coming year include the emphasis on cooperative research in the use of our SANS and high resolution diffraction capabilities for applications in the processing science and durability of metals and ceramics (with the Metallurgy and Fracture and Deformation Divisions). We will also enhance our efforts in collaboration with industrial labs and other CMS Divisions on unique neutron investigations of the structure and properties of high-technology metallic materials and polymers and explore (with NIH and others) the possibility of extending the use of our SANS facility in the study of biological materials and processes. In addition, we anticipate a significant expansion in research using our new time-of-flight neutron spectrometer for high resolution inelastic scattering studies of materials dynamics--particularly in the areas of catalytic reactions on surfaces, hydrogen in metals, and dynamical processes in polymers and zeolytes.

REACTOR OPERATIONS AND SERVICES
Task 12161

Routine round-the-clock operation was resumed following the lengthy shutdown of the previous year. Except for a two-month shutdown to install and connect the new cooling tower and secondary cooling system, reactor operations was almost continuous for the balance of the year. Most of the technical effort this year was directed toward extensive modernization of the reactor and the preparation of safety analyses and environmental appraisal in connection with upgrading the reactor to 20 MW.

In December 1980, application was made to the Nuclear Regulatory Commission to double reactor power to 20 MW and to renew the operating license for another period of 20 years. Extensive documentation in support of the application was prepared and submitted. After publishing its intent to consider the application, the NRC determined that an Environmental Impact Statement would be required because the higher power level put the NBS reactor in a different class. Additional documentation had to be supplied and a public hearing was held on the scope of the Environmental Impact Statement. The NRC is continuing its safety evaluation of the application for upgrade and a decision is expected early in 1982. Once the new license is issued, it will make the NBS reactor the highest powered licensed research reactor in the country. This will permit major expansion of current programs and initiation of new programs not previously possible at the lower power level.

Application and use of the reactor continued to be very extensive and wide ranging. More than 50 major organizations from within and outside NBS are involved. There are now 25 simultaneously operable experimental and irradiation facilities contributing more than 125,000 instrument hours per year.

Reactor Operations
Subtask 1 of Task 12161

T. M. Raby, J. F. Torrence

The reactor operating schedule returned to normal this year following the lengthy shutdown of the previous year due to the shim-arm problem. There was one extended shutdown of two months to complete installation of the new cooling tower and to connect and instrument the new secondary system. The first batch of new high performance elements were loaded into the reactor this year. The new fuel element design has considerably increased operating cycle time resulting in significant cost savings. It is projected that the average fuel element lifetime will increase from the previous 300 operating days to more than 400 operating days. This is more than a 33 percent gain in fuel utilization efficiency. A summary of overall operating statistics for the period July 1, 1980, to June 30, 1981, is presented in the following table. While the on-line time was 65 percent for the whole year, the actual operating efficiency was an outstanding 80 percent if the planned extra shutdown time is excluded. The more than two thousand irradiations made involved tens of thousands of samples and specimens. Overall, the operating record for last year was one of the best in the history of the facility.

NBSR OPERATING SUMMARY FY 80

No. of days at 10 MW	238
On-line time at 10 MW	65%
Average U-235 burnup	52%
No. of Irradiations	2600
Hours of Irradiations	3300
Hours per Irradiation	1.3

Irradiation Services
Subtask 2 of Task 12161

N. A. Bickford, J. H. Ring

Heavy utilization of the reactor for activation analysis and irradiation services resumed after the lengthy shutdown of the previous year. Again multitudes of samples involving foods, drugs, environmental monitoring, geological and mineral studies, forensic investigation, and standard reference materials were irradiated at the NBS reactor.

High precision measurements to detect extremely low level changes in the environment were initiated. A three-fold program is being carried out independently by NBS, other Government agencies, and universities. This involves world-wide sampling for man-made or natural phenomena of specific concern. Included among these is the study of the effect of the eruption of Mount St. Helen on the environment. A comprehensive study of trace and toxic elements has been carried out over the entire length and depth of Chesapeake Bay. Extensive data are currently being evaluated in collaboration with the Environmental Protection Agency.

A new procedure has been developed to determine the platinum concentration in biological materials at the currently natural occurring levels of 10^{-10} to 10^{-11} g/g. This is the first time ever that a certifiable number for platinum has been generated which will be incorporated in several important standard reference materials. This development is a significant breakthrough as it will provide base-line data for monitoring of platinum concentration in the environment and to detect changes as a result of the introduction of catalytic converters in automobiles, for example.

Finally, one of the more important analyses recently completed using the NBS reactor was the examination by the FBI of evidence involved in the shooting of the President.

Engineering Services
Subtask 3 of Task 12161

J. H. Nicklas, R. S. Conway

Besides regular engineering and design services provided to reactor operations, experimenters, and users, the engineering staff was heavily involved in a comprehensive program of reactor modernization. A new high efficiency cooling tower was installed, tested, and is operational, utilizing two speed motor

controls, providing energy conservation. The entire secondary cooling system, including pumps, piping, and controls, was redesigned and modified to provide for more efficient and smoother operation. Old booster pumps were utilized as main pumps to save costs of new pumps. A 24 inch return line was installed from the heat exchangers to the cooling tower to reduce the pressure on the pumps to provide more flow. Two separate suction lines with sumps were installed to increase the suction pressure at the pump intakes to eliminate possible cavitation. This also makes it possible to use one set of pumps to reverse flow through the heat exchangers to clean heat exchanger tubing. The new cooling tower was raised four feet higher than the old tower to further increase the suction pressure on the pumps. Major portions of the reactor console are being redesigned to introduce modern, up-to-date equipment and components. Detector elements such as force balance type transmitters for flow, level, and pressure measurements are being replaced with the latest state-of-the-art strain gauge electronic transmitters. Old recording instruments are being replaced with modern recorders. When the entire modernization program is completed it will provide for greatly improved, more efficient, and reliable operation and will clear the way for the 20 MW conversion as soon as the license amendment is received.

NEUTRON SCATTERING CHARACTERIZATION OF MATERIALS FOR ADVANCED TECHNOLOGIES
Task 12162

This task develops and applies advanced neutron scattering methods and related theoretical analysis for research on the microscopic properties of materials which affect their use in technological applications. Current areas of emphasis include hydrogen in metals, new magnetic and glassy materials, and molecular solids. The neutron inelastic, quasielastic, and magnetic scattering techniques applied provide unique information, e.g., on phase transformations; interatom bonds; electronic structure; sublattice magnetization; hydrogen binding, trapping, and diffusion; and molecular and crystal dynamics. The members of this task (and the following task) are also responsible for establishing and maintaining a center of excellence for neutron scattering and radiographic measurements including a computer-controlled network of ten spectrometers at the reactor. Task scientists couple directly with other NBS and outside groups who require state-of-the-art neutron measurement methods and expertise in their programs. Examples include long-term collaborative efforts with in-house guest workers from Army Materials, Naval Research Laboratory, the Naval Surface Weapons Center, and the University of Maryland on materials for improved microwave transmission and sonar and advanced explosive formulations; cooperative research with industrial scientists (Allied, Bell Labs, IBM) on new classes of materials with potential applications for advanced power transformers, computers, and energy storage; and research on hydrogen in metals and prototype phase transformations in solids with other national laboratories (Argonne National Laboratory, Brookhaven National Laboratory) and universities (University of Illinois, University of Pittsburgh, University of Saarlande, University of Munich). In addition, staff scientists are actively engaged with other Divisions and Centers at NBS in the application of neutron scattering methods for: (1) surface analysis of chemical products and reactions on industrial catalysts, (2) ultrasensitive microscopic analysis of hydrogen in metals, and (3) corrosion in aluminum alloys.

Microscopic Properties of Hydrogen in Metals and Molecular Materials
Subtask 1 of 12162

J. M. Rowe, J. J. Rush, R. C. Casella, S. F. Trevino[1], A. Magerl[2]

[1]Guest Worker, AMRAD
[2]Guest Worker, University of Munich and Institute Laue-Langevin

Hydrogen in Metals. In the area of hydrogen in metals, this group (in collaboration with guest workers from the University of Munich and KFA Julich) has used a new, high-intensity, low-background analyzer for neutron vibrational spectroscopy to extend the sensitivity of atomic scale *in situ* probing of hydrogen in refractory metals by neutron spectroscopy down to the 10 ppm (by weight) level. Using the same technique, they have also, for the first time, succeeded in directly investigating the local environment and potential of hydrogen trapped in a metal by *both* interstitial (O, N) and substitutional (Ti) impurities and have provided a theoretical basis for analyzing these results. In addition, careful measurements of the vibrational lineshapes of H in niobium (30 ppm) as a function of temperature have revealed the existence of precursive clustering of hydrogen far above the $\alpha \rightarrow \beta$ (ordered) phase transition in this metal. These measurements may provide a microscopic explanation for unexplained

ductility transformations previously observed for α-phase refractory metal-hydrogen systems above the α/β phase boundary. The same measurement capabilities have also allowed us to measure the vibrations of tritium in a metal for the first time, despite the fact that neutrons are two orders of magnitude less sensitive to tritium than to hydrogen. Finally, scientists in this subtask have also collaborated with Division 561 in applying neutron spectroscopy to probe low-level hydrogen associated with corrosion in high-strength aluminum alloys. This cooperative effort is continuing in an attempt to correlate these spectroscopic measurements with other data and help establish the mechanism of stress-cracking in these alloys.

Disordered Materials. As part of the continuing research on prototype molecular and disordered materials, this group has established a cooperative research effort with Prof. Zabel of the University of Illinois to study the structure, dynamics, and related microscopic properties of graphite-metal intercalation compounds. During the past year, we have completed the first systematic measurements of phonon-dispersion curves for these compounds and have succeeded in devising a model, including interaction with electronic layers between alkali and graphite planes, which consistently fits the results.

In the past year, we have extended our understanding of mixed crystals both by theory and experiment: first, by measuring the structure of mixed alkali halide-alkali cyanides in the low temperature phase; and second, by initiating computer molecular dynamics calculations on these systems. From this combined approach, we have been able to understand in detail the various interactions in these systems, including the quadrupole-quadrupole, strain mediated, and bare interactions.

Subtask scientists have also carried out, in collaboration with ANL scientists, a unique investigation of a high temperature battery material LiAl by high resolution neutron quasielastic scattering. In spite of an extremely small incoherent scattering from this sample, we were able to directly measure the lithium diffusion constant for this material for the first time and establish the atomic scale mechanism responsible for the fast ion conduction.

Finally, this group has continued its collaboration with the Surface Science and Molecular Spectroscopy Divisions on neutron scattering studies of chemisorbed molecular species and interactions on catalytic surfaces under temperature and gas pressure environments relevant in chemical production. Measurements have been completed on several systems: (1) temperature dependent studies of the chemisorbtion of hydrogen on Raney nickel, including bonding site geometries on the surface; (2) investigation of interactions and decomposition of CO and H_2 coexisting on a catalytic surface; (3) study of temperature dependence of chemisorption and fragmentation of ethylene and acetylene.

Microscopic Properties of Magnetic and Amorphous Materials
Subtask 2 of Task 12162

J. J. Rhyne, J. Lynn[1], H. Alperin[2], R. Erwin[3]

[1]Consultant, University of Maryland
[2]Guest Worker, Naval Surface Weapons Center
[3]Guest Worker (Graduate Student), University of Maryland

This subtask provides a focus for application and improvement of neutron elastic and inelastic scattering techniques for fundamental studies of the microscopic properties of new classes of metallic and magnetic materials (including rare earth and transition metal compounds), many of which exhibit novel properties of potential use in device applications and high-technology products. This research is carried out in close collaboration with industrial labs, universities, and other CMS scientists. Furthermore, the principal scientist of this subtask was one of the leaders of an FY82 CMS competence initiative on the science of nonequilibrium materials, which was selected for presentation to the NBS Director.

During the past year, research emphasis in the subtask was placed on: (1) critical properties and dynamics of alloys of Fe and Ni [e.g., $(Fe_xNi_{1-x})_{0.75}P_{0.16}B_{0.06}Al_{0.03}$] which, for x in the range of 0.3, exhibit unique magnetic phase transitions from paramagnetic to ferromagnetic, and into a "spin-glass" state at low temperature; (2) the influence of hydrogen on the structural and magnetic properties of complex rare earth and actinide manganese compounds; it has been found that the introduction of interstitial hydrogen in these compounds can have profound effects, including the creation or destruction of ordered magnetic phases or spin glass behavior, along with accompanying changes in crystallographic symmetry at low temperature; (3) spin dynamics in amorphous iron-boron alloys which exhibit an Invar anomaly in thermal expansion and the effect of this anomaly on magnetic spin stiffness; and (4) critical behavior and crystal field excitations in rare-earth alloys which exhibit coexistence phenomena of superconductivity and ordered magnetism.

Some highlights of accomplishments during the past year include: (1) established existence of life-time broadened spin waves in the spin glass state of amorphous iron-nickel alloys and suggested a tentative interpretation of these results in terms of a spin-glass order parameter; (2) confirmed the coexistence of long-wavelength periodic magnetic order in superconducting compounds of $HoMo_6S_8$; (3) discovered crystallographic phase change in Y-Mn deuterides and Th-Mn deuterides (from fcc to tetragonal) accompanying their magnetic phase transition. Showed that the Y-Mn compound transforms to a spin glass state rather than becoming antiferromagnetic or nonmagnetic as previously assumed; (4) determined the site magnetization of a newly discovered hexagonal phase of $HoMn_2$; and (5) helped lead a combined Metallurgy-Reactor Radiation Division competence initiative which was one of seven selected by NML for presentation to the NBS Director.

NEUTRON DIFFRACTION AND RADIOGRAPHIC METHODS FOR MATERIALS UTILIZATION AND DURABILITY
Task 12163

This task utilizes the unique role of neutrons (due, e.g., to their deep penetration, sensitivity to light atoms, and well-defined lineshapes for precise structure analysis) in the structural analysis and nondestructive testing of materials. Task members have competences at the forefront of measurement and analysis of materials structure, including concentrated efforts in neutron powder diffraction and profile analysis methods, broad expertise in radiographic measurement technology, and state-of-the-art computer controlled diffraction facilities. This expertise is used to develop advanced neutron diffraction and radiographic methods to provide: (1) precise structure analysis essential for effective use of materials (e.g., in batteries and chemical catalysis); (2) nondestructive reference methods for defects, precipitations, and texture affecting metal product performance, for improved quality assurance, e.g., in pacemaker batteries, composites, and nuclear waste-form materials, and for microstructure analysis of materials in extreme environments; and (3) neutron radiography and beam standards for more accurate and reliable plant and field inspections (e.g., corrosion in aircraft). Current research and measurement activities include cooperative projects with four CMS Divisions (Materials Structure and Durability) and the Center for Radiation Research. This task also directly serves the Offices of Nondestructive Evaluation and Nuclear Measurements. Outside interactions and cooperative research with groups needing advanced neutron methods include NIH, NRL, Army Materials, Navy, FDA, aviation industries, Smithsonian, Allied Corporation, Bell Labs, Medtronics, Inc., Union Carbide, and universities on projects ranging from corrosion detection to the structure of proteins.

Neutron Diffraction Methods and Applications
Subtask 1 of 12163

E. Prince, A. Santoro, B. Mozer, H. J. Prask[1], C. S. Choi[1], A. Wlodawer, L. Sjölin[2]

[1]Guest Worker, AMRAD
[2]Guest Worker, Chalmers Polytechnic Institute and NIH

During the past year, this subtask has made significant advances in both the methods and applications of neutron diffraction. Subtask scientists have expanded cooperative research with other Divisions in CMS (561, 563), industrial labs (Bell Labs, Medtronics, Allied), other national labs (ANL, ORNL, Livermore), and universities (MIT, University of Grenoble). This group, in collaboration with Division 561 and Bell Labs, has utilized the advanced methods recently developed at NBS for powder diffraction lineshape analysis to solve the structure of two ceramic intercalation compounds, $LiReO_3$ and Li_2ReO_3. Further, a new statistical test has been developed to enhance the capability to distinguish between two similar models for complex structures in crystallographic analysis. This new procedure has been successfully applied to allow the determination of the defective structure of $LiTaO_3$ (excess of Ta). This group has also completed the analysis of the structure of prototype pacemaker battery materials ($LiI \cdot H_2O$) and has performed experiments with MIT and ANL on the structure of several other fast-ion conductors. In addition, work has been initiated with CMS metallurgists to use neutron diffraction for detection of undesirable Li-Al phases affecting the durability of the high-strength alloy $LiAl_3$.

In the long-term collaborative program with Army guest workers on the structure properties and NDE of metastable materials, this subtask has (1) solved hitherto undetermined structures of two phases of the explosive NH_4NO_3: (2) utilized combined neutron and x-ray diffraction to provide structural data needed for an understanding of the fundamental properties of cellulose and nitrocellulose; and (3) by computer molecular dynamics, produced the longest time and largest volume simulation yet achieved of shock wave propagation in a liquid and simulated both the stable and metastable chemical behavior of a diatomic solid under thermal stimulus.

Finally, in our NBS-NIH collaborative program on the structure of biological materials, we have completed a determination of the structure of the enzyme ribonuclease-A to 2Å resolution, using both neutron and x-ray data. The success and precision of this structure refinement was considerably enhanced by the new procedures developed by our group for "dynamic masking" to improve signal-to-noise ratios in data from position-sensitive detectors, and by a novel method of refining the crystal orientation matrix on the basis of positions of the stronger crystal reflections. Preliminary analysis of the refined structure has determined the degree of exchange of amide H/D exchange with greater accuracy than that achieved by other methods. Such results can yield information of considerable interest in studies of protein folding.

Radiographic Methods and Standards
Subtask 2 of Task 12163

D. A. Garrett, Y. T. Cheng, W. L. Parker[1]

[1]Guest Scientist

During the past year, this group has initiated or completed several tasks associated with the NDE methods and standards responsibilities of the subtask. First of all, the ASTM Standard "Recommended Practices for Thermal Neutron Radiography of Materials" was adopted by the ASTM in February 1981. In the area of standard neutron beam diagnostics, the feasibility of using the modulation transfer function to define geometric neutron beam characteristics, such as source size and shape, has been demonstrated, and work is continuing in a collaborative effort with the University of Missouri.

In our work with the Nuclear Measurements Program, we have completed a successful demonstration of steady state resonance neutron tomography as a reference method for the inspection of nuclear waste containers and have established a plan for the use of the NBSR irradiation and neutron diffraction facilities for the characterization of nuclear waste-form materials and its behavior under irradiation. Preliminary analysis of a ceramic waste-form before irradiation has been completed. Finally, the Reactor Division has been contacted by the Smithsonian Institution for completion of the engineering design of a potential regional facility for the characterization and authentication of paintings by neutron-activation autoradiography.

ADVANCED NEUTRON METHODS
Task 51102

C. J. Glinka, N. Berk, J. LaRock, J. M. Rowe[1], S. Singhal[2], S. Bai[2]

[1]Competence Leader from Task 12162
[2]IPA Fellow

This task is one of the NBS competence building initiatives whose objective is to develop and maintain state-of-the-art facilities for advanced neutron scattering techniques and enhance the application of these facilities in solid state physics, metallurgy, polymer physics, and biology. The original focus of this initiative is on providing new major facilities for small-angle neutron scattering (SANS) and high-resolution, low-wavevector, inelastic scattering. With small-angle neutron scattering, one can probe structural entities and defects and inhomogenieties on the 10 to 3000Å scale, while high-resolution, inelastic studies allow the observation of dynamic phenomena with characteristic times as low as 10^{-10} sec and spatial regions of 1 to 100Å. The new facilities being created (providing a world-class status for NBS in this area) will serve a wide variety of materials science and measurement programs within NBS, including polymer and surface science, materials microstructure and durability, nondestructive testing, and properties of fluids and solutions. New science and applications to be developed in the future range from unique studies of the structure of polymers and high-technology magnetic glasses to the precise measurement of bulk microstructure in industrial materials and products under environments experienced in production and service. Close cooperation with a number of divisions within CMS and CCP is an essential part of the Advanced Neutron Method task, as is a wide-ranging cooperative research and measurement activity with other Government labs (e.g., NRL, NSWC, NIH) and a number of industrial and university labs (e.g., Union Carbide, Allied, McDonnel, SUNY, University of Maryland, University of Wisconsin).

Summary of Activities. During the past year, we have virtually completed the installation of the NBS small-angle scattering facility. The entire facility has been tested using the original 25 cm x 25 cm area detector, and the first experiments on the new facility have been completed by Charles Han in a study of the effects of uniaxial stress on polymers. The data acquisition system and necessary software for both data collection and analysis are in hand and were used for the polymer work. Testing and installation of the 65 x 65 cm detector were begun when the detector arrived in July 1981. Although the detector is still in the testing phase, initial results are very promising, and we expect to begin taking data again in September 1981. The unique focusing collimator for high resolution work has been tested and works as predicted. Both neutron flux measurements and the polymer scattering experiments indicate that the facility will meet all of its design goals and provide us with a fifty-fold increase in data-taking capability over the previous NBS facility. We plan to enhance the data analysis capability in the near future by completing the network to the VAX computer and by refining the existing data display capabilities of the PDP 11/23 data acquisition system.

Aside from these instrumentation developments, a number of research applications of small-angle scattering and low-wavevector neutron spectroscopy have been initiated or carried out during the past year using our old SANS instrument

and other neutron spectrometers improved as part of the competence initiative. For example, we have completed part of a study of the kinetics of phase decomposition in Ni-Al superalloys in the coherent miscibility gap. Simulating commercial heat treatments, we have followed the precipitation of the $\gamma'Ni_3Al$ phase (which is the strengthening constituent) as a function of aging time. Early results indicate that the kinetics of γ' formation is not linear as previously supposed, but follows a simple power law. In other materials science applications, we have initiated studies with Division 564 on the precipitation of Al_3Li in lithium aluminum alloys and are planning SANS studies with Division 562 on microcracks in structural alloys and ceramics. Research in solid state physics includes studies of critical phenomena and magnetic phase transformations in amorphous alloys and measurement of low-wavevector spin waves in iron-based alloys. Theoretical studies of neutron small-angle scattering phenomena are in progress, including a program to extend and apply modern theories of spinodal decomposition to aging of rapidly quenched metallic alloys.

Other Activities of the Reactor Radiation Division

Invited Talks

Itinerant Electron Magnetism
Conference on Physics of Transition Metals
University of Leeds
Leeds, England
J. W. Lynn
August 19, 1980

Neutron Scattering Studies of Ternary Magnetic Superconductors
International Conference on Ternary Superconductors
Lake Geneva, Wisconsin
J. W. Lynn
September 1980

Neutron Scattering Study of Metal Hydrogen Systems
University of Antwerp
Mol, Belgium
J. M. Rowe
October 1980

Magnetic Neutron Scattering from Rare Earth Amorphous Alloys and Hydrides
Metallurgical Society of AIME
Pittsburgh, Pennsylvania
J. J. Rhyne
October 8, 1980

The Rietveld Method of Powder Pattern Refinement
Pittsburgh Diffraction Conference
University of Pittsburgh
Pittsburgh, Pennsylvania
E. Prince
October 29, 1980

Neutron Scattering Studies of Hydrogen in Metals
Virginia Commonwealth University
Richmond, Virginia
J. M. Rowe
November 1980

Neutron Scattering Studies of Refractory Metal Hydrides
University of Illinois
Urbana, Illinois
A. Magerl
November 1980

Phase Stabilization of Ammonium Nitrate
Workshop on Ammonium Nitrate, Department of Defense
Dover, New Jersey
J. H. Prask
November 1980

Metallic and Structural Properties of $Th_6Mn_{23}D_x$, $Y_6Mn_{23}D_x$, and RFe_2D_x
Symposium on Intermetallic Compounds
University of Pittsburgh
Pittsburgh, Pennsylvania
V. K. Hardman and J. J. Rhyne
November 14, 1980

Magnetic and Structural Properties of $Th_6Mn_{23}D_x$ and $Y_6(Fe_{1-x}Mn_x)_{23}$
Naval Research Laboratory
Washington, D.C.
V. K. Hardman
December 5, 1980

The NBS Reactor Neutron Scattering Facilities
American Physical Society
Phoenix, Arizona
J. J. Rush
March 18, 1981

The Diffractometer Control System at the National Bureau of Standards
American Crystallographic Association
Texas A&M University
College Station, Texas
E. Prince
March 23, 1981

Neutron Scattering as a Probe of Magnetism in Rare-Earth Laves-Phase Compounds and Hydrides
Materials Science Seminar
McMaster University
Hamilton, Ontario, Canada
J. J. Rhyne
March 23, 1981

Neutron Scattering Studies of Dynamics and Phase Transformations in Orientationally Disordered Crystals
American Crystallographic Association
Texas A&M University
College Station, Texas
J. M. Rowe
March 24, 1981

Neutron Scattering Studies of Translation Rotation Coupling in Solids-Alkali Cyanides
Canadian Association of Physics
Dalhousie University
Halifax, Nova Scotia, Canada
J. M. Rowe
June 15, 1981

New Developments in the Use of the Rietveld Method
Institut Laue-Langevin
Grenoble, France
A. Santoro
July 8, 1981

Practical Aspects of the Neutron Diffraction Profile Analysis
Labcratoire de Cristallographie, C.N.R.S.
Grenoble, France
A. Santoro
July 16, 1981

Detection of Impurity Tunneling in Solids via Coherent Phonon Coupling and Direct Neutron Scattering
Blooming, Indiana
R. C. Casella
August 1981

The Relation Between the Rietveld Method and Integrated Intensity Methods in Powder Refinement
Symposium on Neutron Scattering
Argonne National Laboratory
Argonne, Illinois
E. Prince
August 13, 1981

Estimation of Uncertainty in Structure Refinement from Powder Data
XII Congress of International Union of Crystallography
Ottawa, Ontario, Canada
E. Prince
August 20, 1981

Magnetic Phase Transitions in Superconductors
XII Congress of International Union of Crystallography
Ottawa, Ontario, Canada
J. W. Lynn
August 21, 1981

Joint Refinement of Macromolecular Structures with X-ray and Neutron Single-Crystal Diffraction Data
XII Congress of International Union of Crystallography
Ottawa, Ontario, Canada
A. Wlodower
August 22, 1981

Technical and Professional Committee Participation and Leadership

American Crystallographic Association
Apparatus and Standards Committee, E. Prince, Chairman

American National Standards Committee
N-17: Research Reactors, Reactor Physics, and Radiation Shielding,
R. S. Carter, Chairman
T. M. Raby, Secretary

American Nuclear Society
Standards Steering Committee, R. S. Carter, Voting Member
Reactor Operations Division, 1981 Topical Meeting, R. S. Carter,
Session Chairman
ANS-15 Standards for Research Reactors, T. M. Raby

American Physical Society, March Meeting
Magnetic Materials Session, J. J. Rhyne, Session Chairman
Magnetism in Amorphous Systems, J. W. Lynn, Session Chairman

American Society for Nondestructive Testing
Penetrating Radiation Committee, D. A. Garrett, Voting Member
Personnel Qualifications Committee, D. A. Garrett, Voting Member
Research Committee, D. A. Garrett, Voting Member

American Society for Testing and Materials
E-7.05: Nondestructive Testing--Neutron Radiography, D. A. Garrett,
Secretary

Argonne National Laboratory
Consultant, J. M. Rowe
Program Review Committee for the Intense Pulsed Neutron Source,
J. M. Rowe, Chairman

Argonne National Laboratory and Department of Energy
Facilities Review Panel on Intense Pulsed Neutron Sources,
J. M. Rowe, Chairman

Conference on Magnetism and Magnetic Materials
Advisory Committee, J. J. Rhyne, Member
Intermetallics Session, J. J. Rhyne, Session Chairman
Spin Excitations Session, H. A. Alperin, Session Chairman

Department of Energy
Neutron Scattering Review Panel, J. J. Rush, Member

Gordon Conference on Metal Hydrides
The Interticies Occupied by Hydrogen in Intermetallic Compounds Session,
J. J. Rhyne, Discussion Leader

International Conference on Ternary Superconductors
Program Committee, J. W. Lynn, Member

International Symposium on the Electronic Structure and Properties of Hydrogen in Metals
Steering Committee, J. M. Rowe, Member

National Bureau of Standards
Library Committee, R. C. Casella, Subject Specialist
Radiation Safety Task Force Review Panel, J. J. Rush, Member

National Institute of General Medical Sciences
Ad hoc Study Session, A. Wlodower

NATO Conference on Neutron Scattering (to be held in 1982)
Steering Committee, J. J. Rush, Member

Oak Ridge National Laboratory
National Center for Small Angle X-ray and Neutron Scattering,
Program Review Committee, J. J. Rhyne, Member

Rare Earth Research Conference
Proceedings, J. J. Rhyne, Co-editor

XII Congress of the International Union of Crystallography
Macromolecular Structures: Low to High Resolution Refinement Session,
A. Wlodower, Session Co-chairman

Publications

Detection of Impurity Tunneling in Solids via Coherent Phonon Coupling and Direct Neutron Scattering
R. C. Casella
Proc. of International Conference on Phonon Physics (submitted)

The National Bureau of Standards Small Angle Neutron Scattering Spectrometer
C. J. Glinka
Proc. of Symposium on Neutron Scattering (submitted)

Phase Decomposition in th Ni-Rich Side of Ni/Ni_3Al Miscibicity Gap: A Small-Angle Neutron Scattering Study
Satish P. Singhal, H. A. Alperin, F. Biancanello, and H. Herman
Scripta Metall. (submitted)

Powder Neutron Diffraction Study of the Nonstoichiometric Solid Solution of Lithium Tantalate $9LiTaO_3:Ta_2O_5$
A. Santoro, R. S. Roth, and M. C. Austin
Acta Cryst. (submitted)

A Procedure for Joint Refinement of the X-ray and Neutron Single-Crystal Diffraction Data for Macromolecules
Alexander Wlodawer and Wayne A. Hendrickson
Acta Cryst. (submitted)

The Refined Crystal Structure of Ribonuclease A at 2.0Å Resolution
Alexander Wlodawer, Richard Bott, and Lennart Sjölin
J. Biol. Chem. (submitted)

A Robust/Resistant Technique for Crystal Structure Refinement
W. L. Nicholson and E. Prince
Acta Cryst. (submitted)

Small Angle Neutron Scattering Study of the Nonlinearity of Spinodal Reaction in a Symmetric Au-60 at % Pt Alloy
Satish P. Singhal, H. Herman, and G. Kostorz
Proc. of International Conference on Solid-Solid Phase Transformation (submitted)

Theory of Neutron Scattering from Hydrogen in Metals Involving Transitions to Excited Tunnel-Split States
R. C. Casella
Phys. Rev. B (submitted)

Tritium Vibrations in Niobium by Neutron Spectroscopy
J. J. Rush, A. Magerl, J. M. Rowe, J. M. Harris, and J. L. Provo
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Use of the Pearson Type VII Distribution in the Neutron Profile Refinement of the Structures of $LiReO_3$ and Li_2ReO_3
A. Santoro, R. J. Cava, D. W. Murphy, and R. S. Roth
Proc. of Symposium on Neutron Scattering (submitted)

Comments on "Triplet Exciton Annihilation and Triplet Spin Relaxation in Molecular Crystals"
J. Rosenthal, L. Yarmus, and N. F. Berk
Phys. Rev. B (in press)

Comparison of Profile and Integrated Intensity Methods in Powder Refinement
E. Prince
J. Appl. Cryst. (in press)

Comparison of the Fits of Two Models to the Same Data Set
E. Prince
Acta Cryst. (in press)

Improved Technique for Peak Integration for Crystallographic Data Collected Using Position-Sensitive Detectors: A Dynamic Mask Procedure
Lennart Sjölin and Alexander Wlodawer
Acta Cryst. (in press)

Improvement of the Quality of the Data Collected Using a Position-Sensitive Detector
Alexander Wlodawer and Lennart Sjölin
J. Nucl. Instrum. and Methods (in press)

Magnetic and Structural Properties of $Th_6Mn_{23}D_x$ and $Y_6Mn_{23}D_x$
V. K. Hardman, J. J. Rhyne, E. Prince, H. K. Smith, S. K. Malik, and W. E. Wallace
The Rare Earths in Modern Science and Technology, Vol. III (in press)

Magnetic Properties of Cubic and Hexagonal $HoMn_2$
J. J. Rhyne, V. K. Hardman, S. K. Malik, and W. E. Wallace
The Rare Earths in Modern Science and Technology, Vol. III (in press)

Refinement of the Crystal Orientation Matrix for the Flat-Cone Diffractometer
Alexander Wlodawer, Lennart Sjölin, and A. Santoro
J. Appl. Cryst. (in press)

Refinement of 2-Nitroguanidine by Neutron Powder Diffraction
C. S. Choi
Acta Cryst. (in press)

Structural Aspects of Lithium Insertion in Oxides: Li_xReO_3 and $Li_2FeV_3O_8$
A. Santoro, R. J. Cava, D. W. Murphy, and R. S. Roth
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Coherent Neutron Scattering Study of the Vibrations of Interstitial Deuterium in α-$VD_{0.7}$
J. J. Rush, J. M. Rowe, C. J. Glinka, N. Vagelatos, and H. E. Flotow
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S. P. Singhal
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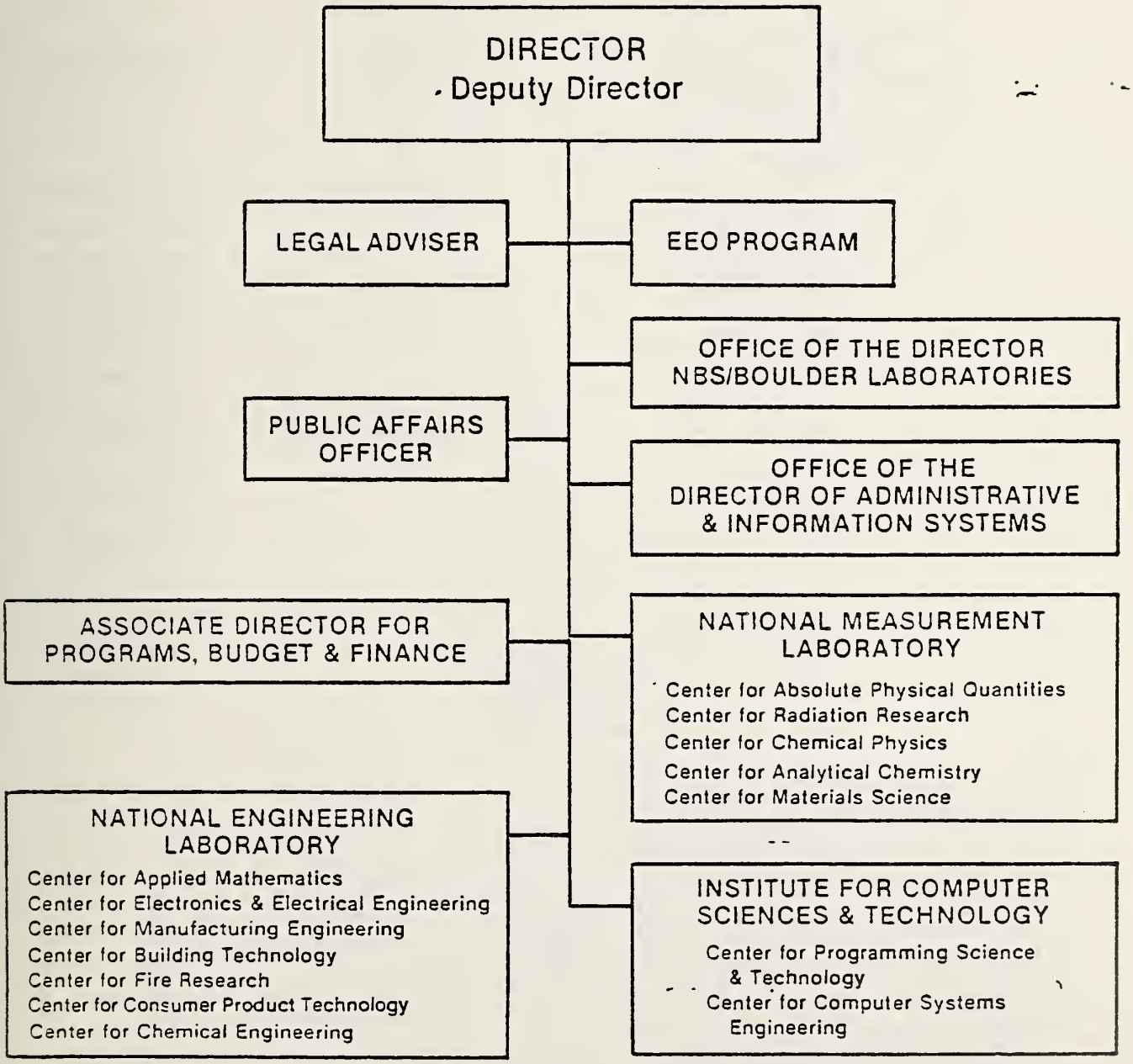

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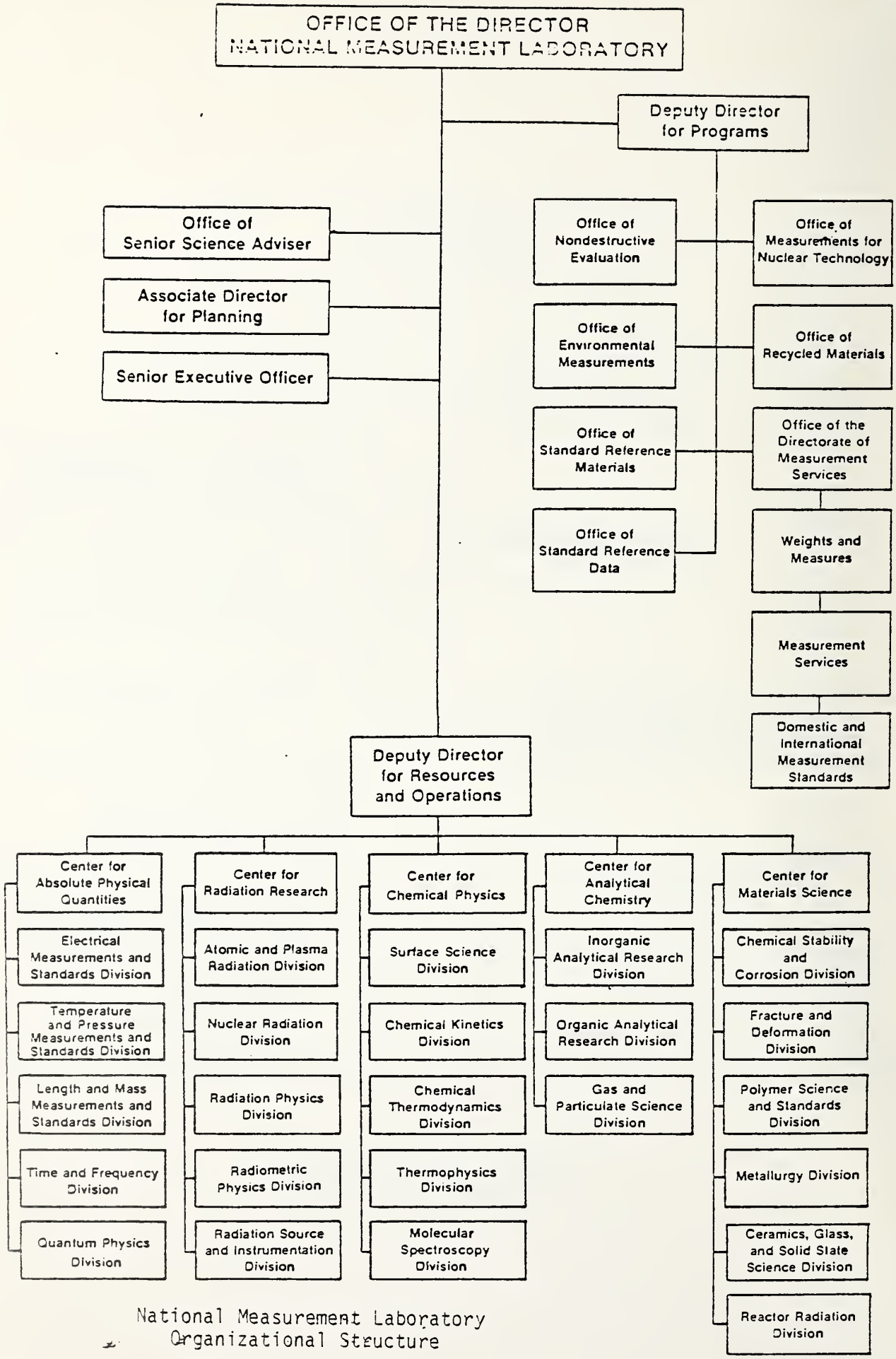
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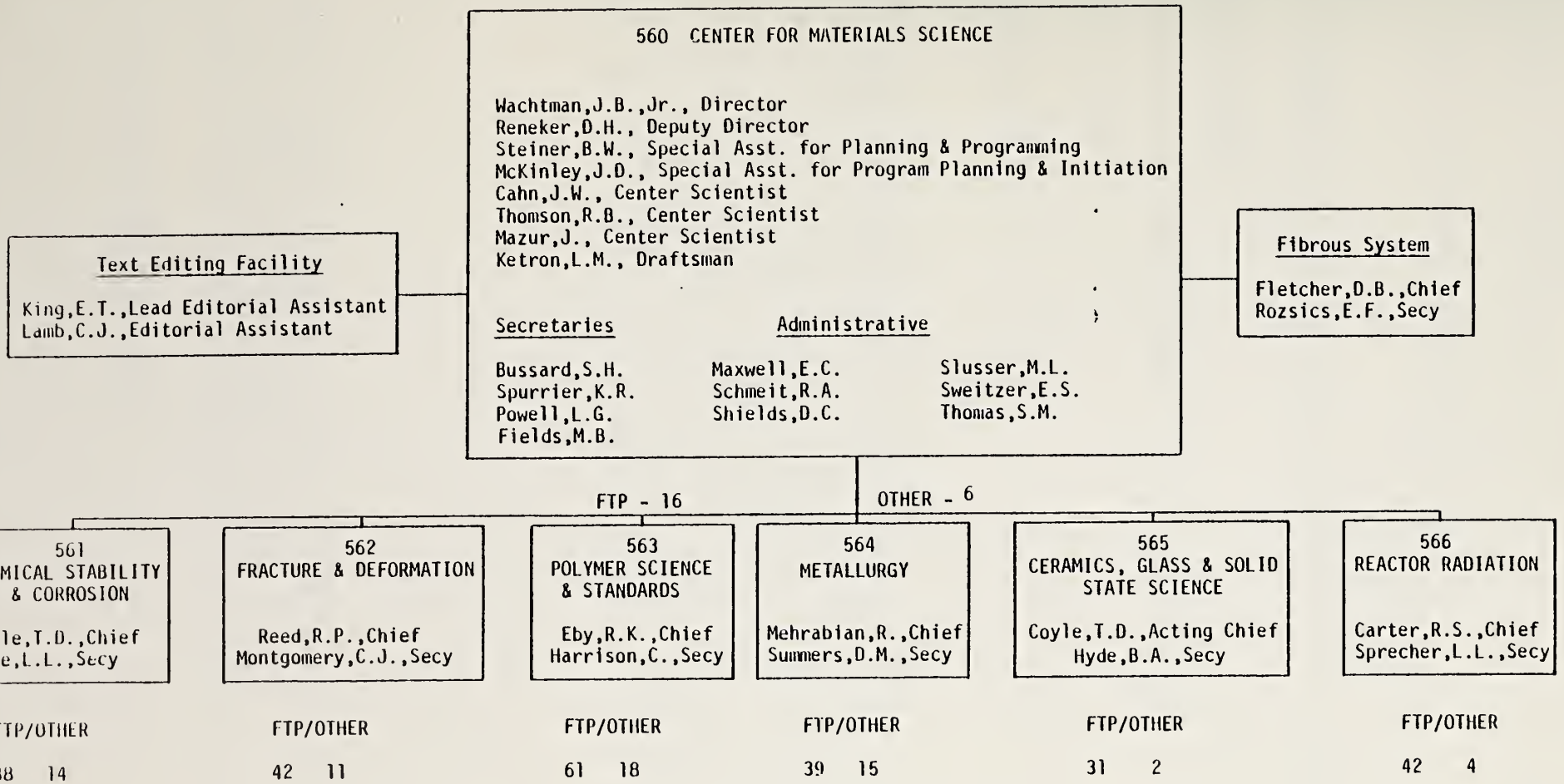

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12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons.)

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